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Illinois State Geological Survey, Urbana

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16. ABSTRACT

The aqueous solubility, adsorption, mobility, microbial degradation, and volatility of polychlorinated biphenyls (PCBs) were studied under laboratory conditions. The dissolution of Aroclor 1242 in water required five months to reach equilibrium. Generally, the water-soluble fractions of the PCB fluids were richer in the lower chlorinated isomers than in the original mixture of isomers in the fluid. The solubilities of Aroclor 1016, 1221, 1242, and 1254 were 906 ppb, 703 ppb, and ≈70 ppb, respectively.

A simple linear relation described the adsorption of water-soluble PCBs by five earth materials and their low-temperature ashes. An adsorption constant (K) unique to each adsorbent was obtained. The adsorption was strongly correlated to the total organic carbon (TOC) content and surface area of the earth materials. TOC was the dominant of these two earth material properties by a ratio greater than three to one.

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ATTENUATION OF WATER-SOLUBLE POLYCHLORINATED BIPHENYLS BY EARTH MATERIALS

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FOREWORD

The Environmental Protection Agency was created because of increasing concern by the public and government about the dangers of pollution to the health and welfare of the American people. Noxious air, foul water, and spoiled land are tragic testimony to the deterioration of our natural environment. The complexity of that environment and the interplay between its components require a concentrated and integrated attack on the problem.

Research and development—that necessary first step in solving a problem—involves defining the problem, measuring its impact, and searching for solutions. The Municipal Environmental Research Laboratory develops new and improved technology and systems to preserve and treat public drinking water supplies, to minimize the adverse economic, social, health, and aesthetic effects of polution and to prevent, treat, and manage waste water and solid and hazardous waste pollutant discharges from municipal and community sources. This publication is one of the products of that research; it is a vital communications link between the researcher and the community.

Results are reported from laboratory investigation of the capacity of earth materials to attenuate polychlorinated biphenyls (PCBs) from waters. These results are applicable to the design of treatment systems, earth material liners for sanitary landfills, and to the land disposal of municipal and hazardous wastes.

Francis T. Mayo, Director
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ABSTRACT

The aqueous solubility, adsorption, mobility, microbial degradation, and volatility of polychlorinated biphenyls (PCBs) were studied under laboratory conditions. The dissolution of Aroclor 1242 in water required five months to reach equilibrium. Generally, the water-soluble fractions of the PCB fluids were richer in the lower chlorinated isomers than in the original mixture of isomers in the fluid. The solubilities of Aroclor 1016, 1221, 1242, and 1254 were 906 ppb, 3516 ppb, 703 ppb, and ∿70 ppb, respectively.

A simple linear relation described the adsorption of water-soluble PCBs by five earth materials and their low-temperature ashes. An adsorption constant (K) unique to each adsorbent was obtained. The adsorption was strongly correlated to the total organic carbon (TOC) content and surface area of the earth materials. TOC was the dominant of these two earth material properties by a ratio greater than three to one.

The mobilities of several PCBs in silica-gel, silica sand, seven soils, and a coal char were measured with several leaching solutions using the soil thin-layer chromatography technique. The PCBs remained immobile when leached with water or landfill leachate, but were intensely mobile when leached with organic solvents. The mobilities were strongly related to the solubilities of the PCBs in the leaching solvent. The mobilities of PCBs in soils leached with carbon tetrachloride were highly correlated to the soil TOC content.

The degradation of water-soluble Aroclor 1242 by mixed cultures of soil microorganisms occurred in a short period of time. The lower chlorinated isomers were degraded more easily than the higher chlorinated isomers. The rates of degradation ranged from the monochloro isomers, which degraded 100 percent within 6 hours, to the tetrachloro isomers, which averaged 42 percent degradation after 15 days. The predominant organisms found in the mixed cultures were *Alkaligenes odorans, Alkaligenes denitrificans,* and an unidentified bacterium.

The volatility of PCBs from water was studied in the presence of soluble humic acid and suspended soil. Adsorption of PCBs by the soil and humic acid reduced the total amounts of PCBs volatilized. The volatilization of PCBs from pure water agreed with theoretical predictions that the half-life of Aroclor 1242 stripped from water would be about 6 hours. Higher chlorinated PCB isomers were found to be less soluble in water, preferentially adsorbed by soil materials, less mobile in soil, less degradable by microorganisms, and less volatile from water than lower chlorinated isomers. Thus, higher chlorinated isomers would be less mobile and more persistent in the environment than lower chlorinated isomers.

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SECTION 1

INTRODUCTION

Polychlorinated biphenyls (PCBs) is a generic term applied to certain mixtures of chlorinated organic compounds. PCBs have become the subject of much discussion recently because of their effect on the environment. They persist and accumulate in the environment and have been found in samples of air, water, soil, sediments, fish, birds, and mammals (including humans) all over the world. PCBs are not acutely toxic, but several chronic effects have been observed. Therefore, PCBs have been considered a significant hazard to human health as well as to the environment (Gustafson, 1970, 1972; EHRC, 1976).

CHEMICAL STRUCTURE

PCBs belong to a class of aromatic chlorinated organic compounds that comprise complex heterogeneous mixtures of very closely related isomers. The basic biphenyl structure is shown in Figure 1. PCBs are made by substituting chlorine atoms for one or more of the hydrogen atoms at the numbered positions of the biphenyl structure. Possible chlorine substituted biphenyl isomers number 209, but commercial preparations contain less than the total possible; about 103 have been identified in various samples (Widmark, 1967; 1968). The different commercial preparations may vary from batch to batch with regard to the specific composition of the mixture of chlorinated biphenyl isomers (EHRC, 1976; Lloyd et al., 1976).

MANUFACTURE AND INDUSTRIAL USES

PCBs have been manufactured in the United States since 1929 by the Monsanto Chemical Company; an estimated 800 million pounds have been produced since that time. In 1970, the year of peak production, more than 85 million pounds of PCBs were produced in the United States alone, 57 percent of which was in the form of Aroclor 1242 (HEW, 1972). An estimated one-half million pounds

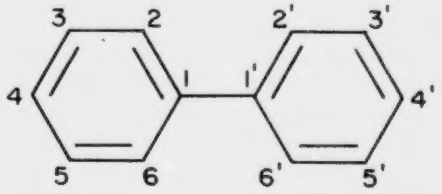

Figure 1. BIPHENYL STRUCTURE: Positions 2 to 6 and 2' to 6' indicate ten possible positions for chlorine substitution. Different amounts of chlorine substitution form the various PCBs.

per year of PCBs were imported into the United States from foreign manufacturers (EHRC, 1976).

The sole United States manufacturer of PCBs was the Monsanto Chemical Company located near East St. Louis, Illinois. Monsanto has marketed its PCB products in the United States under the trade name AROCLOR. A four-digit numbering system was used to identify various Aroclors. The first two numbers, 12, specified polychlorinated biphenyls, and the last two numbers referred to the approximate percentage of chlorine in the mixture. For example, Aroclor 1242 means a PCB mixture with 42 percent chlorine by weight (EHRC, 1976; Nisbet and Sarofim, 1972). A product called Aroclor 1016 came into use after 1971 which did not follow the above numbering sequence. This product contained approximately 41 percent chlorine and was an attempt by Monsanto to produce an Aroclor that could be used in the same applications as Aroclor 1242; it contained fewer of the higher chlorinated isomers and was thus more degradable and less persistent in the environment (Tucker, Litschgi, and Mees, 1975). Aroclors can also be classified by the average number of chlorine atoms per molecule. Thus, Aroclor 1232, 1242, 1248, 1254, 1260, and 1262 correspond to di-, tri-, tetra-, penta-, hexa-, and hepta-chlorobiphenyls, respectively. Other trade names for PCB products produced by foreign manufacturers include: KANECHLOR and SANTOTHERM (Japan), PHENOCLOR and PYRALENE (France), FENCLOR (Italy), CLOPHEN (Germany), and SOVOL (Russia) (EHRC, 1976; Lloyd et al., 1976).

PCBs come in both solid and liquid forms and have properties appropriate to a wide range of industrial applications. In resin form they were used as protective coatings, plasticizers and extenders, sealers in waterproofing compounds and putty, asphaltic materials, printing inks, and synthetic adhesives. In liquid form they were used as dielectrics, hydraulic fluids, thermostats, cutting oils, extreme pressure lubricants, grinding fluids, and heat transfer media. As solids they were used to impregnate carbon resistors, as sealers, and as impregnating agents for electrical apparatus. With few exceptions, other than environmental concerns, the unique properties of PCBs qualify them as the best chemical known to make capacitors, transformers, hydraulics, gas turbines, and vacuum pumps work efficiently and safely (EHRC, 1976).

In 1971, because of environmental concerns, Monsanto voluntarily stopped production of Aroclor 1260 and restricted the sale of other PCBs to only "closed" systems. Closed systems include PCB-containing insulating fluids used in electrical transformers and capacitors; these two applications account for essentially all the current use of PCBs in the United States (ANSC, 1976). On October 5, 1976, Monsanto announced that it would cease to manufacture and distribute PCBs by October 31, 1977. A timetable set by the United States Environmental Protection Agency (EPA) called for gradual phasing out of PCB manufacturing by January 1, 1979, and a ban on all PCB processing or distribution in commerce by July 1, 1979 (ES&T, 1977). These steps should reduce the introduction of PCBs into the environment in the future, but millions of pounds of PCBs still exist in transformers and capacitors still in service. The environmentally safe disposal of these fluids will continue to be of concern for more than a decade.

ENVIRONMENTAL EFFECTS

PCBs were largely ignored as environmental contaminants until 1966 when Jensen (1966) reported PCB contamination of fish, eagles, and humans. PCBs still did not attract much concern as hazardous chemicals until the incidence of contaminated cooking oil in Japan (Risebrough et al., 1968) and of contaminated chicken feed in the United States (Duke, Lowe, and Wilson, 1970). Laboratory studies with animals have shown that PCBs can cause enlargement of the liver, induction of hepatic microsomal enzymes, reproductive failures, gastric disorders, skin lesions, and tumors in birds and mammals (Nelson et al., 1972).

The best documented case of toxic effects of PCBs in humans is the 1968 "Yusho" incident in Japan. About 2,000 Japanese people experienced lesions of the skin, facial swelling, and neurological disorders. The individuals with the highest dosages had nausea, lassitude, anorexia, impotence, and hematuria. The severity of the symptoms were directly related to the quantities of PCBs ingested. Placental transfer of PCBs had occurred in pregnant women and had adversly affected the fetuses. The toxic effects noted were similar to those reported in animal studies (Nelson et al. , 1972; EHRC, 1976).

Several studies with animals have shown that fatty tissue accumulates about 10 times more PCBs than liver and more than 100 times more than blood, heart, kidney, and brain (Burse et al.,1974; Grant, Phillips, and Villeneuve, 1971; and Curley et al., 1971). A study with refuse workers found that 81 percent had detectable levels of PCBs in their blood (Hammer et al., 1972).

PCBs have found their way into the marine and terrestrial environment. Risebrough et al. (1968) noted that PCBs, along with the chlorinated hydrocarbon pesticides, have become the most widespread and ubiquous synthetic pollutants in the global ecosystem. They also noted that PCBs induced hepatic enzymes that degrade estradial, which leads to aberrations in calcium metabolism, such as weak, thin egg shells.

Because PCBs are fat soluble and poorly metabolized, they have entered the food chain and accumulated in the adipose tissues of fish, birds, and mammals, including humans (Jensen et al., 1969; Hammond, 1972; Solly and Shanks, 1974; Harvey and Steinhauer, 1975). The biological magnification of PCBs that have entered the food chain seems to occur by a factor of 10 to 100 at each step. Fish and aquatic organisms accumulate PCBs by a factor of 10^4 over concentrations in the ambient waters. Predators at the top of the food chain can accumulate PCBs by a factor of 10^7 over the concentrations found in the ambient waters (EHRC, 1976). The major problem with regard to PCB intake by man is that he resides at the top of most food chains. Man can therefore amass substantial amounts of PCBs although only trace levels are present in the waters of lakes and streams.

A two-year study of Lake Michigan showed that fish with the highest fat content contained the highest levels of PCBs (Schacht, 1974). Other studies have shown that salmon taken from Lake Michigan in 1974 contained PCBs in excess of the 5 ppm FDA tolerance level. Lake trout were reported to contain PCBs as high as 43.8 ppm, and carp contained levels as high as 51.6 ppm (EHRC, 1976).

The highest concentrations of PCBs are found in fish that come from the Hudson River in New York. Fish taken from below the General Electric capacitor manufacturing plant contained PCBs in the range of 17 to 78 ppm; one sample of rock bass contained 350 ppm (Ahmed, 1976). The bed and bank sediments in a 40-mile reach of the river were estimated to contain more than 400,000 pounds of PCBs, and concentrations as high as 5,600 ppm were found (Maslansky et al., 1978).

Old electrical equipment has been discarded by many companies and the PCBs have discharged into the atmosphere and waterways. PCBs are somewhat volatile, and the migration of PCBs through air is considered to be one of the basic mechanisms by which the ubiquitous presence of PCBs in nature occurs (Persson, 1971). An average fallout rate of 40 to 80 $\mu g/m^2$/year of PCBs over continental North America was reported by the Panel on Hazardous Trace Substances (Nelson et al., 1972).

DISPOSAL AND SOIL ATTENUATION

One problem of disposal involves the high costs and fees for transporting PCB wastes to regional incinerators or approved landfills compared to simply discarding the wastes. The costs at disposal sites that specially treat or incinerate wastes may be as high as a dollar per gallon or more. The costs for land burial are generally between 5 to 10 cents per gallon (Troise and Kahn, 1978).

Incineration is considered the safest method for disposal of PCB wastes, but this method is extremely costly and has some operating difficulties. PCBs do not burn readily; the operating conditions of the incinerator must be carefully controlled to prevent the reentry of PCBs into the environment in the stack gases (Duvall and Rubey, 1977; Moon, Leighton, and Huebner, 1976).

Nisbet and Sarofim (1972) estimated the rate of PCB disposal in dumps and landfills in North America in 1970 to be 18,000 tons per year. In view of this, land disposal of PCBs and related materials has concerned many people (Jordan, 1977; Henderson, 1978) because surprisingly little is known about the mobility of PCBs in soil systems.

The hydrophobic characteristic of PCBs make them easily adsorbed from aqueous solution onto available surfaces; the amount of PCBs being adsorbed depends on the nature of the surface (Haque, Schmedding, and Freed, 1974; Lawrence and Tosine, 1976). Haque and Schmedding (1976) studied the adsorption characteristics of three selected PCB isomers by several adsorbents and provided evidence that adsorption increases as the number of chlorine atoms on the isomer increases.

Iwata, Westlake, and Gunther (1973) studied the persistence of PCBs in six California soils. Preferential disappearance of some gas chromatograph

(GC) peaks was evident and recovery of Aroclor 1254 was related to the organic-matter content of the soil. In a separate study of PCB uptake by carrots, 97 percent of the residue was found in the peel and very little translocation into the plant tissue. Again, the lesser chlorinated biphenyls were slowly dissipated and the more highly chlorinated biphenyls were not appreciably affected (Iwata, Gunther, and Westlake, 1974).

Tucker, Litschgi, and Mees (1975) percolated water through soil columns containing PCBs. In the worst case, less than 0.05 percent of the added Aroclor 1016 was leached; they concluded that PCBs are not readily leached from soils. Similarly, Scharpenseel, Theng, and Stephan (1978) found that very little leaching of PCBs occurred and that the PCBs recovered from the soil were associated with the soil organic matter.

Briggs (1973) reported that adsorption of unionized organic compounds by soils was related to the organic-matter content of the soil and to the octanol/water partition coefficients of the compound. On the basis of the octanol/water partition coefficients for PCBs, he predicted that they would be immobile in soils.

Lidgett and Vodden (1970) analyzed waters around a sanitary landfill for PCBs and found the contamination levels to be below their detection limits of 4 ppb. Similarly, Robertson and Li (1976) used GC/Mass Spectrometry techniques and failed to detect PCBs in ground water. Hesse (1971) reported that runoff from landfills was only a minor source of PCB contamination to the environment. More recently, Moon, Leighton, and Huebner (1976) reported that levels of PCBs in ground water in the vicinity of 11 sanitary landfills were below detection (<1 ppb), but that low levels of PCBs were found in waters from monitoring wells at several industrial PCB disposal sites and lagoons. They concluded from analyses of water and splitspoon soil samples that PCBs were present in most leachates from land disposal sites and that PCBs have a strong affinity for soil. Gresshoff, Mahanty, and Gortner (1977) have also reported that PCBs have a high affinity for soils. Leis et al. (1978) studied PCB migration in ground water from 12 dredge disposal sites in the upper Hudson River Valley of New York. They concluded that the velocity of the front of PCB advance was about 2 orders of magnitude slower than the velocity of the ground water flow. They further concluded that inputs of PCB that were due to migration through ground water were negligible in comparison to other inputs of PCBs.

The information presently available indicates that PCBs have a strong affinity for soil and that the nature of the surface, the organic matter content, and the chlorine content and/or hydrophobicity of the individual PCB isomers are factors affecting adsorption. Quantitative data on the adsorption capacities and factors affecting PCB adsorption by earth materials are needed to assess the impact of soil attenuation mechanisms for restricting PCB mobility in the environment.

MICROBIAL DEGRADATION

The above studies suggest that the interaction of PCBs with soil particles is an important attenuation mechanism. Another potentially important mechanism is the degradation of PCBs by microorganisms.

Biphenyl Degradation

Various species of microorganisms that can degrade biphenyl have been reported. Lunt and Evans (1970) were the first to report the microbial degradation of biphenyl. The microorganisms used were gram-negative bacteria found in soil. They reported that biphenyl was degraded to 2,3-dihydroxybiphenyl. This compound was then degraded to a α-hydroxy-β-phenylmuconic semialdehyde and then to phenylpyruvate.

Catelani et al. (1971, 1973) reported that *Pseudomonas putida* could degrade biphenyl. The biphenyl was degraded to 2,3-dihydroxybiphenyl and further degraded to benzoic acid and 4-hydroxy-2-oxovaleric acid.

Gibson et al. (1973) reported a *Beijerinckia* species that could degrade biphenyl to 2,3-dihydroxybiphenyl. They also reported that the intermediate in this step, *cis*-2,3-dihydroxy-1-phenylcyclohexa-4,6-diene was formed by bacteria, whereas the *trans* isomers were formed in mammals.

PCB Degradation by Pure Cultures

Wallnofer et al. (1973) isolated a soil fungus, *Rhizopus japonicas*, which converts 4-chlorobiphenyl to 4-chloro-4'hydroxybiphenyl.

Ahmed and Focht (1973a, 1973b) reported the degradation of several PCB isomers by two species of *Achromobacter*. They isolated the two species from sewage, the first by biphenyl enrichment and the second by 4-chlorobiphenyl enrichment. They reported that the products produced by these two species were different; this suggests different metabolic pathways for degradation. They showed that degradation of the unsubstituted aromatic ring was preferred. This, and the observation that no dechlorination occurred, lead to a buildup in chlorobenzoic acids. Recently, Omori and Alexander (1978) reported that certain alkanes can be dehalogenated. If dehalogenation, along with degradation, can occur, then PCBs can be broken down into small nonchlorinated compounds. Kaiser and Wong (1974) reported the isolation of some microorganisms that degraded PCBs into metabolites that contained neither chlorine nor oxygen. This is quite unusual because the PCBs are degraded aerobically and therefore should be oxidized and should contain oxygen.

Baxter et al. (1975) measured PCB degradation by a species of *Nocardia* and a species of *Pseudomonas*. With the *Nocardia* species they reported 88 percent and 95 percent degradation for 52 and 100 days, respectively. With the *Pseudomonas* species they reported 76 and 85 percent for the same periods. Both studies were done with Aroclor 1242. They also did work with single PCB isomers and in these studies found that PCB isomers with up to 6 chlorines could be degraded to some degree and that the pattern of chlorine substitution determines the ease of degradation. They also found that the two species would degrade some isomers differently; for example, the *Nocardia* could not degrade 4,4'-dichlorobiphenyl in 121 days, whereas the *Pseudomonas* species degraded it about 50 percent in 15 days. They also reported a form of cometabolization, in that some isomers degraded more slowly when present as the only carbon substrate, but degraded more rapidly when in a mixture of isomers or when biphenyl was present. An example of this was 2,5,4'-trichlorobiphenyl. When alone this isomer degraded only 15 percent in 73 days; however, with biphenyl the degradation was 60 percent in 73 days.

Furukawa and Matsumura (1976) isolated an *Alkaligenes* species from a lake sediment by enrichment with biphenyl. The PCBs were degraded in two steps. The first step was the formation of a yellow product, identified as a chlorinated derivative of 2-hydroxy-6-oxo-6-phenylhexa-2,4-dienoic acid. This compound was then broken down into chlorinated benzoic acids. In addition, the isomers with 4'-chlorine produced longer lasting yellow intermediates. PCB isomers with chlorines on only one of the rings were degraded more easily than those with chlorines on both rings. They also found that lower chlorinated isomers were more easily degraded and that isomers with up to five chlorines could be degraded.

A later study by Furukawa, Tonomura, and Kamibayashi (1978) with *Alkaligenes* and *Acinetobacter* used 31 different PCB isomers and showed similar results. They found that isomers with 3,6 or 2,2' chlorines were poorly degraded. They also reported less degradation as the number of chlorines per molecule increased. The two species showed about the same amount of degradation of each isomer except for 2,4,6-trichlorobiphenyl. Several trichlorobiphenyl isomers could be degraded almost completely in less than three hours by these microorganisms.

Sayler, Shou, and Colwell (1977) isolated a species of *Pseudomonas* from sea water that degraded PCBs. They obtained between 9 and 39 percent degradation of Aroclor 1254 in 22 days, the percentage depending on the starting concentration. In 60 days they found between 63 and 84 percent degradation, again the percentage depending on the starting concentration. At 22 days, the lowest degradation was at the lowest concentration, 10 μg/L; at 60 days the lowest degradation was at the highest concentration, 1000 μg/L. Ballschmitter, Unglert, and Neul (1977) proposed several schemes for the microbial breakdown of PCBs into various metabolites, including chlorinated benzoic acids.

It has been known for some time that PCBs could be degraded by mammals and birds. Sundstrom, Hutzinger, and Safe (1976) presented a review of the metabolism of PCBs in animals. Hutzinger, Safe, and Zitko (1974) also presented a review of PCBs in both animals and microorganisms. Sayler, Shou, and Colwell (1977) noted that the degradation of PCBs in animals could actually be caused by the action of the intestinal microbiota.

PCB Degradation in Sewage

Many PCBs end up in sewers, either through spills or dumpings, and then go into activated sludge systems. Tucker, Litschgi, and Mees (1975) worked with a continuously fed activated sludge unit. At a feed level of 1 mg/48 hrs., they reported 100 percent degradation of biphenyl, 81 percent degradation of Aroclor 1221, 33 percent degradation of Aroclor 1016, 26 percent degradation of Aroclor 1242, and 15 percent degradation of Aroclor 1254. With Aroclor 1221, only the 3-, 4-, and 5-chlorine isomers were not degraded.

Mihashi et al. (1975) reported 50 percent PCB degradation in activated sludge and that the degree of degradation decreased as chlorine substitution increased.

Herbst et al. (1977) studied the fate of two radiolabeled isomers of PCB, 2,5,4'-trichlorobiphenyl and 2,4,6,2',4'-pentachlorobiphenyl. They determined that the two isomers were poorly degraded by the activated sludge. In addition, most of the PCBs ended up in the activated sludge and not in the supernatant. Jordan (1977) reported on the case of Williams, Indiana; activated sludge containing up to 300 ppm PCBs was used as fertilizer and harmed both the people and the wildlife of the area.

Inhibition by PCBs

PCBs also inhibit the growth of microorganisms that have not been acclimated to PCBs. Bourquin and Cassidy (1975) reported that a sizeable proportion of estuarine bacteria are sensitive to PCBs. They pointed out that if PCBs were present in large amounts, the normal microbial heterotrophic activity could be disrupted.

Murado, Tejedor, and Baluja (1976) reported that Aroclor 1254 would inhibit the formation of mycelium of *Aspergillus flavus*. They also found that no degradation of PCBs occurs in these cultures. Blakemore and Carey (1978) reported the inhibiting of growth of two marine bacteria by low concentrations of Aroclor 1254. They found that the inhibition was dose dependent and that respiration was not inhibited. Blakemore (1978) also reported the inhibition of nucleic acid synthesis in a marine bacteria and subsequent inhibition of growth in these bacteria.

It is clear from the above studies that PCBs are somewhat degradable and may come under attack by soil microorganisms. If a mixed culture of soil microorganisms could be enriched in organisms that could degrade PCBs at a significant rate, it would then be feasible to use biological processes to treat PCBs; or PCB wastes could be inoculated with the culture before land disposal, assuming that the organisms would be competitive in the particular environment.

ANALYTICAL METHODOLOGY

Quantitative Analysis

The analysis of PCBs has been a matter of estimation; attempts at quantitation of PCBs have most often been done by measuring the heights of major gas-liquid chromatographic peaks. Koeman et al. (1969), semiquantitatively measured only one of the major peaks, Skrentny, Hemken, and Dorough (1971) used two, and Zitko (1971) used three quantification peaks. Reynolds (1971) applied Koeman's method and took an average of two or more major peaks in the mixture as the standard. Hansen et al. (1971) averaged the heights of five major peaks. Likewise, PCBs also have been quantified by summing the areas of all the individual peaks obtained by gas-liquid chromatographic analyses. Jensen et al. (1969) quantitatively estimated the concentration of PCBs by the total peak areas. Armour and Burke (1970) measured

PCBs in terms of Aroclor 1254 by using the total area of the peaks. Risebrough, Reiche, and Alcott (1969) multiplied a factor derived from measurements of standard PCB solutions by a microcoulometric detector to the areas measured by electron capture detector (ECD). Beezhold and Stout (1973) used a mixed standard to quantify PCBs.

All the gas-liquid chromatography used for the above studies employed an electron capture detector on the chromatograph. Unfortunately, the electron capture detector does not respond quantitatively the same for all PCB isomers, as noted by Rote and Murphy (1971), Cook (1972), Wiencke and Roach (1972), and Beezhold and Stout (1973). A procedure designed to overcome this problem was to perchlorinate the PCB sample (Berg, Diosady, and Rees, 1972; Armour, 1973; Berg, Rees, and Ali, 1978; Burkard and Armstrong (1978). In the perchlorination procedure, the PCBs were reacted with antimony pentachloride ($SbCl_5$) to form decachlorobiphenyl (DCB). The advantage of the perchlorination procedure is that all the chlorinated biphenyl is detected as one peak by the GC, thus giving improved quantitation and speed of analysis. In addition, the ECD is more sensitive to the higher chlorinated compound. Studies by Trotter and Young (1975), however, showed problems in the perchlorination reaction with $SbCl_5$ that were due to trace amounts of bromine in $SbCl_5$ in the form of $SbBrCl_4$. Because the bromine has a higher affinity for biphenyl than the chlorine, bromonanochlorinated biphenyl (BNCB) is formed during perchlorination. The BNCB peak would show up in a GC trace after the DCB peak. Further studies are needed to improve the quantitation of PCBs by this procedure.

Improvements in PCB analysis can be made by the use of open tubular glass capillary columns which have liquid phases custom-coated on the walls of the column. The apparatus and dynamic-coating procedures of Grob (1975) and Grob, Grob, and Grob (1977) can also be used.

Generally, liquid phases for capillary gas chromatography can be divided into apolar, medium polar, and polar phases. Polar phase columns were notoriously short-lived. Apolar liquid phases (OV-17, OV-101, SE-30, etc.) were widely accepted as the most efficient coatings because of their longer life; these generally are the ones available commercially. Because of the aromatic characteristics of PCBs, a polar phase is needed to achieve maximum separation efficiency. The merit of the glass-surface pretreatment methods given by Grob is that polar phases such as Emulphor ON-870 can be coated on the glass and used for PCB analysis with increased column life. In addition, the column can easily be regenerated. When a column has deteriorated to an unusable quality, a cleaning solution can be passed through the column to wash out the residual liquid, and the column can then be recoated. In the case of silicone liquid phases, such as OV-17, OV-101, and SE-30, the regeneration step is not possible.

Mobility Measurements

The technique of determining pesticide mobility in soils by soil thin-layer chromatography, or soil TLC, was introduced by Helling and Turner (1968). Since the introduction of the technique, the mobility of a large number of pesticides and radionuclides in a variety of soils has been tested

(Helling, 1971a, 1971b, 1971c; Reeves, Francis, and Duguid, 1977). Soil TLC is a laboratory technique that uses soil as the adsorbent phase and developing solvent such as water, leachate, and organic solvent in a TLC system. The system is relatively simple and yields quantitative data on the mobilities of chemical constituents in soils that appear to correlate well with trends noted in the literature (Helling and Turner, 1968; Briggs, 1973; Reeves et al., 1977).

CONCLUDING REMARKS

An exact value for the solubility of PCBs in water is difficult to determine because PCBs are mixtures of substituted isomeric biphenyls that have different numbers of chlorine atoms. The structure of the PCB molecule was shown in figure 1 to illustrate the various possible combinations of chlorine substitution. Of the 209 possible isomers, about 103 usually occur in commercial PCB mixtures (Widmark, 1978). PCBs are hydrophobic and are only slightly soluble in water. Isomers with lower chlorine substitution have been shown to be preferentially dissolved in water (Zitko, 1971; Hoover, (1971). Another important factor in the quantitative analysis of PCB solubility is that PCBs dissolve in water very slowly. Therefore, there must be a time-dependent study before the absolute value of the water solubility of PCBs can be obtained (Haque and Schmedding, 1976). PCBs are also subject to volatilization (Zitko, 1970) and photodecomposition (Ruzo, Zabik, and Shiretz, 1972; Safe and Hutzinger, 1971; and Hutzinger, Safe, and Zitko, (1972). In view of the above difficulties, care must be taken when designing experimental protocols and interpreting data.

The information presently available regarding soil attenuation mechanisms indicates that PCBs have a strong affinity for soil and are somewhat degradable by microorganisms. There is no evidence that ground water around sites containing relatively low levels of PCBs, such as sanitary landfills, has become contaminated with PCBs; however, surface and ground waters around some industrial disposal sites and around lagoons containing relatively large quantities of PCBs have become contaminated by leaching PCBs. The mechanisms of transport of PCBs in the biosphere and the mechanisms of attenuation in soil are essentially unknown. Data on the factors affecting PCB attenuation by earth materials and the microbial degradation of PCBs would provide a useful basis for determining waste treatment methods, for predicting PCB migration under landfills, and for selecting and designing future disposal sites.

The purposes of the present project were (a) to conduct a literature review of pertinent information on the attenuation of PCBs in soil materials and their behavior in the environment; (b) to measure the adsorption capacity of selected earth materials for pure PCBs and PCB wastes; (c) to evaluate quantitatively the effects of biological degradation, volatilization, time, organic carbon content, and adsorbent structure on attenuation of PCBs; (d) to use this data to develop a mathematical model that will allow prediction of PCB adsorption and mobility; (e) to measure quantitatively the aqueous solubility of PCBs; and (f) to further develop analytical procedures that will allow quantitative measurement of PCBs contained in aqueous solutions.

SECTION 2

CONCLUSIONS

Studies of the aqueous solubility, adsorption, mobility, microbial degradation, and volatility of PCBs have led to the following conclusions:

1. The rate of dissolution of Aroclor 1242 and a used capacitor fluid (Aroclor 1242 impregnated) in water were essentially identical and required 5 months under the experimental conditions employed in this study (the rate of dissolution of PCBs probably depends on the stirring rate).

2. The solubility of individual PCB isomers was greatly reduced in the Aroclor mixture where other PCB isomers were present than when compared to their individual solubilities.

3. The water-soluble fraction of PCBs was richer in the low-chlorinated isomers than that in the original PCB fluids.

4. Used capacitor fluids can be assumed to be the same as Aroclor 1242 in terms of the pattern of isomer distribution in the original fluid and the water-soluble fractions, in solubility, and presumably in its behavior in the environment. Age and the "burn out" process do not appear to alter appreciably the Aroclor 1242.

5. Some particular isomers in Aroclor 1242 were relatively soluble compared to their counterparts with similar degrees of chlorination. They were identified as 2-mono-; 2,4'-di-; 2,5,2'-tri-; 2,3,2'-tri-; 2,5,4'-tri-; 2,5,2',5'-tetra-; 2,4,2',5'-tetra-; 2,4,2',4'-tetra-; 2,3,2'5'-tetra-; and 2,4,3',4'-tetra-chlorobiphenyl.

6. The solubilities of Aroclor 1016, 1221, 1242, 1254 and capacitor fluid at room temperature were 906 ppb, 3516 ppb, 703 ppb, ∿70 ppb, and 698 ppb, respectively.

7. A simple linear relation described the total adsorption of PCBs from aqueous solution by earth materials and yielded an adsorption constant (K) unique to each adsorbent.

8. There were no significant differences between adsorption of water-soluble Aroclor 1242 and a water-soluble used capacitor fluid (Aroclor 1242 impregnated) by any of the five earth materials.

9. Adsorption of PCBs by the five earth materials; medium-temperature coal char (*MTC*), high-temperature coal char (*HTC*), Catlin soil (*CS*), montmorillonite clay (*MC*), and Ottawa silica sand (*OS*) followed the series

$$MTC > HTC > CS > MC > OS.$$

10. Higher chlorinated isomers were preferentially adsorbed over lower chlorinated isomers.

11. Very highly significant (.001 level) linear correlations were found between K and total organic carbon (*TOC*); K and CO_2-surface area (*SA*); and K, *TOC*, and CO_2-*SA*. Poor correlations were found between K and N_2-*SA*; and K and ethylene glycol-*SA*. It was concluded that PCB molecules were unable to penetrate the interlayer region of montmorillonite to be adsorbed.

12. *TOC* and CO_2-*SA* were the most important properties of earth materials controlling PCB adsorption; *TOC* was the dominant property by a factor greater than three.

13. Aroclor 1242, Aroclor 1254, and capacitor fluid remained immobile in soils when leached with water or leachate from the Du Page landfill on soil thin-layer chromatography (*TLC*) plates, but were highly mobile when leached with carbon tetrachloride. Dicamba showed the reverse trend.

14. The mobilities of the PCBs and Dicamba in thin-layers of soil materials and silica-gel were highly related to their solubilities in the solvent with which the *TLC* plates were being leached.

15. The higher chlorinated Aroclor 1254 was less mobile in soils leached with carbon tetrachloride than the lower chlorinated Aroclor 1242.

16. There was a highly significant (.001 level) correlation between the mobility of PCBs in the soil and the soil *TOC* content.

17. The degradation of water-soluble Aroclor 1242 by mixed cultures of soil microorganisms occurred to a large extent in a short period of time. Degradation rates varied from monochloro isomers that were degraded 100 percent within 6 hours to tetrachloro isomers that averaged 42 percent degradation after 15 days.

18. In general, lower chlorinated isomers were more easily degraded than higher chlorinated isomers. Position of chlorine substitution affected the rate of PCB degradation.

19. The predominant organisms found in the mixed cultures were *Alkaligenes odorans*, *Alkaligenes denitrificans*, and an unidentified bacterium.

20. Volatilization of PCBs from aqueous solution was reduced by the presence of soil and the reduction was due to preferential sorption onto the soil particulates.

21. Substantial binding of PCBs by soluble humic substances occurred, especially for the higher chlorinated isomers, but such binding was less effective than that by soils in reducing volatilization from aqueous solution.

22. Volatilization of PCBs from a landfill leachate can be expected to be reduced substantially because of the high content of particulates and high concentration of humic substances. Volatilization favored the lower chlorinated isomers.

23. Higher chlorinated PCB isomers were less soluble in water, preferentially adsorbed by soil materials, less mobile in soil, less degradable by microorganisms, and less volatile from water than lower chlorinated isomers.

SECTION 3

RECOMMENDATIONS

The results and conclusions formulated from this study generally dealt specifically with solubility and attenuation of PCBs from pure aqueous solutions. The presence of soluble salts and organic materials in water, as frequently occurs in landfills and the environment, could drastically alter some predictions of PCB attenuation.

Soluble salts reduce the aqueous solubility of hydrophobic organic compounds such as PCBs. The magnitude of the "salting out" effect and its influence on attenuation of PCBs by earth materials should be determined. Likewise, the effect of organic solvents and waste streams of various categories needs to be examined.

The effects of organic solvents on increasing the mobility of PCBs in soils were dramatically illustrated during this study; however, the effects of organic solvents on PCB adsorption remain unknown. These effects may be of particular significance where montmorillonite clays are involved. The organic solvent may expand the clay layers and allow access to the interlayer surfaces; this should substantially increase the amounts of PCBs that are adsorbed as compared to their adsorption from aqueous solution, where PCBs were apparently restricted to adsorption on the external surfaces only. The interrelationship of surface area and organic carbon content of soils needs further elucidation to improve predictions of PCB migration through soils.

With regard to microbial degradation, it is recommended that studies be carried out on the effects of soil on the degradation process. Substantial and rapid degradation was observed in aqueous solutions, however, selective adsorption of PCBs by the soil and competition from native soil organisms may drastically alter the degradation. It is anticipated that PCB degradation rates in soil will be substantially lower than those observed in solution cultures.

The studies of volatility of PCBs were limited in scope. More work is needed on the effects of soil properties and conditions on volatilization before accurate predictions could be made of the flux of PCBs in soils due to volatilization.

Thus, these multiple interactions of the properties of soil and the chemistry of wastes must be considered when making predictions of the environmental impact of PCBs. A major task still before us is the utilization of quantitative data on the chemistry of soil to make predictions of PCB migration through soil materials. It is therefore recommended that further studies involve a cooperative effort between soil chemists, ground-water hydrologists, and modelers to implement by computer the prediction process and to identify possible gaps in knowledge that may still bar the successful prediction of long-term PCB migration through soil materials.

SECTION 4

MATERIALS AND METHODS

PCB MATERIALS AND EXTRACTION PROCEDURES

The PCBs Aroclor 1016, 1221, 1242, and 1254 were obtained from the Monsanto Chemical Company and were used without further purification. The capacitor fluid was drained directly from a burned-out 50-KVA capacitor manufactured in 1966 and originally impregnated with Aroclor 1242. This capacitor was supplied by Illinois Power Company and was scheduled for disposal in a landfill. We believe that this fluid is representative of the type of PCB wastes that are normally disposed of in landfills.

A 20-mL volume of the individual PCB fluids was placed in a 5-gallon glass carboy, which had been cleaned and baked at 450° C overnight. The carboy was filled with water that had been passed through a mixed bed exchange resin and an activated carbon bed and was finally distilled in glass. The carboy was then sealed with an aluminum-wrapped rubber stopper and was wrapped with aluminum foil and masking tape to protect it from exposure to light. The solution in the carboy was agitated gently with a magnetic stirring bar coated with Teflon. Gentle agitation was used to avoid breaking the PCB fluids into a fine suspension. Water samples were collected from the carboys at regular intervals, and 100 mL aliquots of the PCB-water solution were filtered through glass wool plugs tightly packed into the stems of glass funnels. The first 100-mL aliquot was used to saturate the PCB adsorption

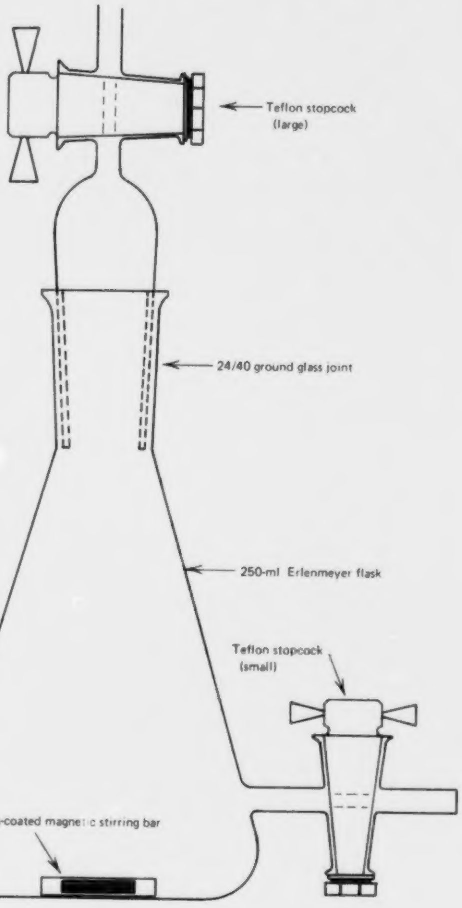

Figure 2. Modified Erlenmeyer flask for extraction of PCBs from aqueous sample

capacity of the glass wool and was discarded. Subsequent aliquots were then used in the studies. The filtrates were then extracted with three 5-mL portions of either carbon tetrachloride or hexane (distilled in glass grade, Burdick and Jackson Laboratories, Inc., Muskegon, MI) in a specially designed extractor, which is shown in figure 2. Samples to be analyzed by the perchlorination procedure were extracted with carbon tetrachloride. The samples to be analyzed by capillary column techniques were extracted with hexane. The extracts were passed through a florisil column containing approximately 75 percent florisil (Floridin Co., Tallahassee, FL) and 25 percent Na_2SO_4. This was done to remove any water or polar materials that may have been co-extracted from the samples (Reinert, 1970; Curley et al., 1975). (The application of florisil, silica gel, and alumina to clean up other contaminants from PCBs has been used successfully in many studies [Reynolds, 1969; Snyder and Reinert, 1971; Berg, Diosady, and Reese, 1972; and Ahnoff and Josefsson, 1975].)

The column was 5 mm I.D. x 50 mm long and was first flushed with solvent. The sample was then passed through the column and collected in a 10 mL volumetric flask. The column was further eluted with at least one bed volume of solvent which was subsequently added to the flask until exactly

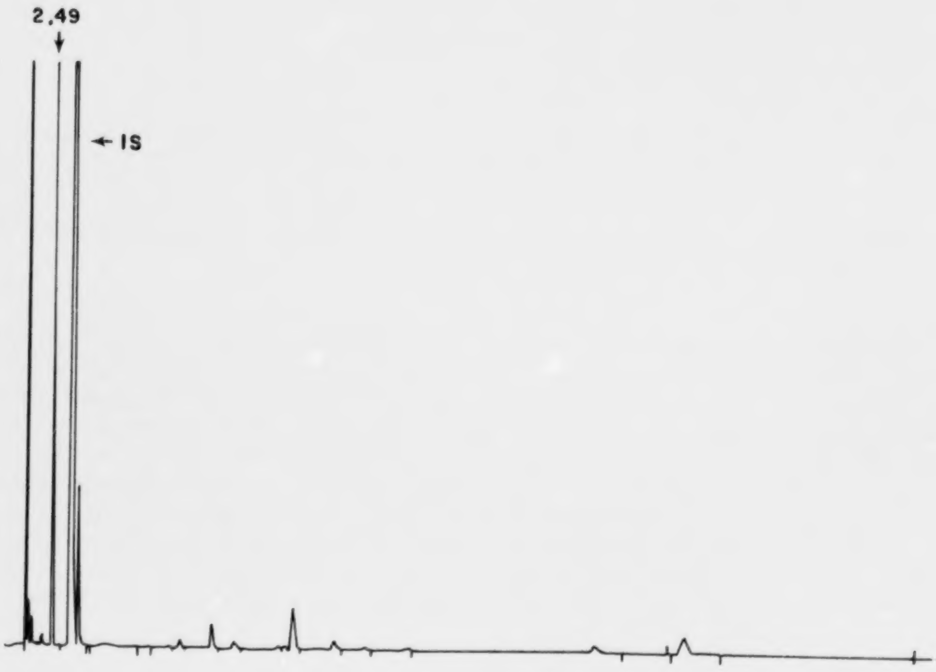

Figure 3. A GC chromatogram of internal standard (tribromobenzene) in hexane

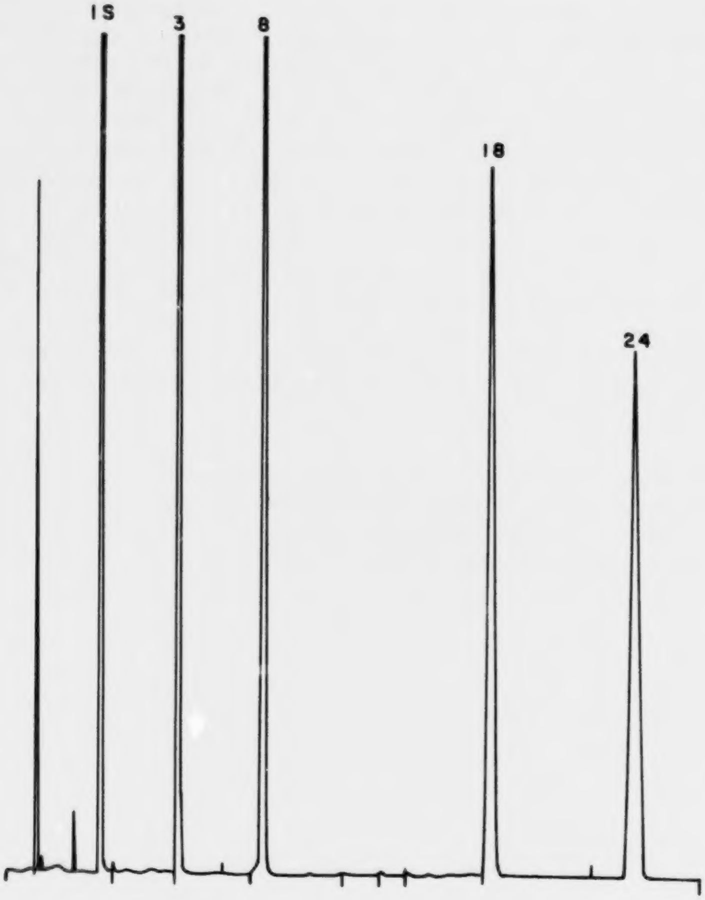

Figure 4. A chromatogram of internal standard (IS) and four different PCB isomers; 4-mono- (peak 3); 2,4'-di-(peak 8); 2,5,4'-tri- (peak 18); and 2,4,2',4'-tetra-chlorobiphenyl (peak 24)

10 mL had been collected. The hexane filtrates from the florisil columns were then spiked with tribromobenzene as an internal standard for quantitative analysis. The possible interferences from the solvents and internal standard were checked. Figure 3 is a chromatogram of a hexane solution containing a high concentration of internal standard. The peaks in the chromatogram illustrate some of the impurities present in the reagents that do not normally show up on chromatograms of samples or a standard (Fig. 4). Figure 4 is a chromatogram of the internal standard and four PCB isomers. The major impurity, shown in Figure 3 as a peak at retention time 2.49 min., elutes before any PCB peaks and therefore does not interfere with the analyses.

Aqueous samples from adsorption studies with earth materials were extracted with 20 mL of either carbon tetrachloride or hexane in three aliquots of 10, 5, and 5 mL each. The first extract was then placed in a 10 mL Kuderna-Danish (K-D) evaporator (Kontes Glass Co., Vineyard, NJ) and was concentrated to approximately 1 mL in a 100°C water bath by using NaCl crystals as boiling chips. The second extract was added to the K-D and the concentration process was repeated. The third extract was combined with the condensed sample to give a final volume of about 6 mL. The 6 mL of condensed sample was then passed through a florisil column as described above and was analyzed for PCBs.

PCB Materials Used in Mobility Study

The PCBs and Aroclors 1242 and 1254 were obtained from the Monsanto Chemical Company (St. Louis, MO) and were used without further purification. The ^{14}C labeled compounds were obtained from New England Nuclear Corporation (Boston, MA). Gas chromatographic (GC) traces of the ^{14}C labeled compounds were identical to those of the Aroclor 1242 and 1254, therefore it was assumed that there were no significant differences in the respective compounds and that the ^{14}C labeled PCBs and Aroclors would behave similarly in studies of mobility. The specific activities of Aroclor 1242 and 1254 were 0.119 m Ci/mg and 0.096 m Ci/mg, respectively.

The used capacitor fluid described previously was also used in this study.

EARTH MATERIALS

Adsorbents

The adsorbents used in the PCB adsorption study were Ottawa sand (OS), montmorillonite clay (MC), Catlin silt loam soil (CS), Illinois No. 6 coal charred at 1800°F (HTC), and the same coal charred at 1200°F (MTC). The two chars were soaked and rinsed with distilled-deionized water and then oven dried at 110°C overnight. The coal chars are impure forms of activated charcoal and were selected for study because of their potentially high adsorption capacity for PCBs and their possible use as liners for disposal sites accepting organic wastes. The sand, clay, and soil represented the major soil materials and offered a range of chemical and physical characteristics. These are presented in Tables 1 and 2. The chemical and physical characterization was performed as described by Griffin and Shimp (1978).

The organic matter content of the adsorbents was varied by using the low-temperature ashing (LTA) technique for bituminous coals described by Gluskoter (1965) and Kuhn, Fiene, and Harvey (1978). An aliquot of each sample was ashed except for Catlin soil for which three aliquots were ashed, each for different time intervals. The changes in organic matter content and surface area that are due to ashing are shown in Table 1.

Surface areas were measured by three methods, each selected to provide different information about the surface characteristics of the adsorbents. The BET gas adsorption method was used as described by Thomas and Frost (1971). Both N_2 and CO_2 were used as adsorbates. The third method was ethylene glycol adsorption as described by Bower and Gschwend (1952).

TABLE 1. Characteristics of earth materials used in adsorption studies.

			Surface area						
Adsorbent	pH	CEC (meq/100g)	N_2 (m^2/g)	CO_2 (m^2/g)	Ethylene glycol (m^2/g)	Sand (%)	Silt (%)	Clay (%)	Organic carbon (%)
Ottawa silica sand (OS)	5.2	0.0	0.5	0.4	<1	100	0	0	$<.01$
Montmorillonite clay (MC)	7.0	85.0	23.2	20.1	885	0	0	100	0.93
Montmorillonite clay (LTA)			23.9	20.2					0.13
Catlin silt loam AP (CS)	7.1	18.1	10.1	26.5	68	11.6	60.9	27.2	4.73
Catlin, 6 hr. LTA			12.6	25.4					4.37
Catlin, 12 hr. LTA			11.4	24.5					3.64
Catlin, 336 hr. LTA			16.3	23.8					1.84
Coal char (1200°F) (MTC)	7.3	9.6	1.6	253	55	-	-	-	74.04
Coal char (1200°F) (LTA)			2.1	214					64.00
Coal char (1800°F) (HTC)	7.0	1.7	3.4	44	68	-	-	-	76.62
Coal char (1800°F) (LTA)			10.0	120					32.14

TABLE 2. Chemical characteristics of earth materials used in adsorption studies.

Constituent	High temp. char (%)	Med. temp. char (%)	Catlin Ap soil (%)	Montmorillonite clay (%)	Ottawa silica sand (%)
Al_2O_3	3.77	2.93	9.63	13.32	0.19
CaO	0.59	0.68	0.98	5.05	0.07
Cl	0.01	0.04	-	-	-
Fe_2O_3	3.04	2.52	4.07	2.73	0.09
P_2O_5	$<$ 0.01	0.01	0.09	0.05	$<$ 0.01
K_2O	0.41	0.29	1.90	0.34	0.01
SiO_2	12.93	9.36	69.50	59.98	97.38
TiO_2	0.25	0.19	0.74	0.23	0.01
MgO	$<$ 0.01	$<$ 0.01	0.01	3.48	$<$ 0.01
Na_2O	0.15	0.12	0.68	-	-
S	2.89	3.28	0.06	0.02	0.01
	(ppm)	(ppm)	(ppm)	(ppm)	(ppm)
Cl	-	-	72	-	38
V_2O_5	30	31	64	19	$<$ 9
MnO	86	54	543	30	$<$ 2
Na_2O	-	-	-	695	27
Sn	$<$50	$<$50	$<$50	$<$ 50	$<$ 50
Cu	117	45	45	43	4.3
Co	$<$ 2.4	$<$ 2.4	9.6	$<$ 2.4	$<$ 2.4
Ni	19	8.6	22	6.8	$<$ 1
Be	1.6	1.3	3.1	1.4	$<$ 1
Cr	26	24	62	27	$<$ 1
Mo	6.8	6.3	4.0	$<$ 3.4	$<$ 3.4
Zr	60	22	237	98	80
Pb	$<$ 2	$<$ 2	16	8.2	$<$ 2
Zn	36	23	72	19	$<$ 1.6
F	125	95	160	435	$<$ 10

Soil Materials

Soil materials representing a wide range in characteristics were selected for use in the mobility study. These included a pure silica sand, seven soils, and medium-temperature (1200°F) coal char. The materials and some of their chemical and physical characteristics are listed in Table 3. All the soil materials were ground in a mortar with pestle and screened (28 mesh) before use.

ADSORPTION STUDIES

All glassware was cleaned with tap water, rinsed with distilled-deionized water, and baked in an oven at 450°C for at least 8 hours. Weighed amounts of adsorbent were placed into 125 mL brown serium bottles. An aliquot of PCB-saturated water was taken from the 5-gallon carboy described earlier and filtered through glass-wool plugs that were packed tightly into the stems of glass funnels. A 60-mL volume of filtrate was then added to the reaction bottle. The bottle was covered with a sheet of baked aluminum foil and sealed by a teflon-coated septum and a crimp-cap (Wheaton Laboratory Products, Millville, NJ, and Pierce Chemical Co., Rockford, IL). The

TABLE 3. Characteristics of soil materials used in PCB mobility studies.

			Surface area						
Material	pH	CEC (meq/100g)	N_2 (m^2/g)	CO_2 (m^2/g)	Ethylene glycol (m^2/g)	Sand (%)	Silt (%)	Clay (%)	Organic carbon (%)
Ava Silty clay loam	4.5	13.1	28.3	28.9	55	2	69.6	28.4	1.18
Bloomfield Loamy sand	5.7	0.8	1.7	2.2	2.0	82	10	8	0.21
Catlin Silt loam	7.1	18.1	10.4	26.5	68	11.6	60.9	27.2	4.73
Catlin Loam	8.7	4.7	11.5	11.2	17	35.9	43.5	18.5	0.57
Cisne Silt loam	5.9	8.0	6.1	13.0	23	13.8	70.8	14.8	1.30
Coal char (1200°F)	7.3	9.6	1.60	253	55	-	-	-	74.04
Drummer Silty clay loam	6.7	29.4	22.1	29.1	103	17.9	49.5	31.6	2.17
Flanagan Silty clay loam	6.6	23.3	12.6	32.8	93	5.4	65.2	29.4	2.62
Ottawa Silica sand	5.2	0.0	0.5	0.4	<1	100	0	0	<0.01

brown bottles protected the PCB solutions from photodecomposition during the adsorption process and the crimp seals prevented volatilization losses during the reaction period. The bottles were shaken overnight in a water bath at 25 ± 0.5°C.

The bottles were removed from the shaker and placed directly into a Model JS-7.5 rotor and centrifuged at a constant temperature of 25 ± 1°C in a Beckman Model J-21B centrifuge for 5 minutes at 6000 rpm. They were then removed from the centrifuge head, the seals were broken, and 40 mL of the clear supernatants were pipetted for PCB analysis.

The effect of reaction-time on PCB adsorption was studied by using the methods described above. Two series of samples were prepared, each containing water saturated with Aroclor 1242 and a fixed amount of montmorillonite clay. The two dosages of clay were 167 mg/L and 1667 mg/L. The bottles were removed from the shaker after various time intervals and analyzed for their PCB content. The results showed that a shaking time of 8 hours was sufficient to reach equilibrium conditions. Therefore, all samples were shaken overnight to ensure equilibration and for convenience of analysis. Blanks were carried through all experiments to determine the background levels of contamination of the adsorbents with PCBs and to evaluate the adsorption of PCBs onto the surfaces of the glassware.

The amount of adsorption was determined from the difference between the initial concentration and the equilibrium concentration multiplied by the volume of solution. A blank was subtracted and the amount adsorbed by each sample was computed on a unit basis by dividing by the dry weight of the adsorbent.

PCB MOBILITY STUDIES

The mobilities of Aroclor 1242, Aroclor 1254, and Dicamba were studied using the soil TLC technique described by Helling (1971a). Dicamba, a pesticide of known high mobility, was used as an internal standard. The adsorbent was slurried with water until moderately fluid, and was applied with a spreader to a clean glass plate (20 cm x 20 cm) that had been washed with ethanol and acetone. The adsorbent was spread to a thickness of 0.5 mm and then air dried. A horizontal line was scribed with a stainless steel spatula at 12 cm above the base to stop solvent movement; vertical lines were scribed 2 cm apart to separate the various treatments. The radioactive compounds were spotted on 2 cm from the base and leached 10 cm with a developing solvent. The activity of the ^{14}C labeled PCB that was spotted was 22,000 d.p.m. (84 ng for 1242, 104 ng for 1254). The plate was immersed in 0.5 cm of solvent in a closed glass chamber and was removed when the wetting front reached the horizontal line. Leaching was thus ascending chromatography. The developed plate was then removed and air dried. A piece of 8 x 10 inch medical x-ray film was placed in direct contact with the developed plate for a period of 2 weeks. The resulting autoradiograph indicated the relative movement of the compound, which was measured as the frontal R_f of the spot or streak. The R_f value is defined as the ratio of the distance the compound moved relative to the distance the solvent moved. The R_f value is a quantitative indication of the front of PCB movement and a reproducible index of mobility.

The soil TLC plates were developed with three leaching solvents; distilled-deionized water, Du Page leachate, and carbon tetrachloride. Distilled water was further purified by passage through a Milli-Q (Millipore Corp.) reagent grade (> 10 megohm resistance) water system. The organic solvents were glass-distilled from Burdick and Jackson (Muskegon, MI) and the leachate was collected from the Du Page County, Illinois sanitary landfill (well MM-63). The site description and well location were described by Hughes, Landon, and Farvolden (1971) and the chemical characterization of the Du Page leachate by Griffin and Shimp (1978). The three leaching solvents were each extracted with hexane and analyzed for trace contamination of PCBs by using standard GC techniques and were found to be free from contamination.

The mobilities of the two Aroclors and Dicamba were also measured on silica-gel (GF-254, type 60, Brinkmann Instr., NY) TLC plates leached with a variety of solvents. The solvents used were deionized H_2O; Du Page leachate; carbon tetrachloride; benzene; acetone; 80:20 water:acetone; methanol; 15:85 water:methanol; and 9:91 water:methanol.

To confirm the data obtained from autoradiographs, zonal extractions were done on several lanes spotted with PCB. A given lane was divided into 12 equal segments starting from 1.5 cm below the origin to 10.5 cm above the origin. The soil in each segment was carefully transferred to a clean graduated centrifuge tube to which 0.5 mL of 1:1 $C_2H_5OH:H_2O$ was added; 4 mL of nanograde hexane was used as the extracting solvent. The ethanol mixed with water at the soil surface and provided a more polar phase than the hexane whereby the PCB in the soil could be more effectively extracted into the hexane layer. The soil suspensions were sealed with aluminum foil, mixed with a vortex mixer for a few seconds, and left to stand for an hour. This procedure was repeated three times to allow complete extraction of PCB from the soil, and a recovery of 99.7 ± 1.5 percent of PCB was obtained. The soil suspension was then centrifuged at 2500 rpm for 5 minutes. The final volume of hexane was recorded. One mL of the radioactive PCB-hexane solution was pipetted into a scintillation vial containing 10 mL Dioxane scintillation fluid (7 g PPO, 0.05 g POPOP; 120 g Naphthalene in 1 L Dioxane), and the activity was counted for 10 minutes in a Packard Tri-Carb Liquid Scintillation Spectrometer and the results corrected for quench. In the case of nonradioactive PCBs (capicitor fluid), the hexane extract was analyzed for PCB by standard GC techniques. The conditions for the gas chromatographic analysis were as follows:

Instrument: Varian 2100 series Sc_3H electron capture detector

Column: 6 ft glass column 2.5% OV-210 and 1.5% OV-17 on 60/80 Supelcoport G.C. Bondx

Injection port temperature: 220°C

Column temperature: 200°C

Detector temperature 250°C

Carrier gas: N_2, flow 15-20 mL/min

Electrometer: range 10^{-10} amp/mv, attenuation 16

MICROBIAL DEGRADATION

Isolation of Mixed Cultures

Three mixed cultures of microorganisms were isolated by biphenyl enrichment from three different soil and sediments. To isolate the mixed cultures, 5 g of soil or sediment and 0.1 g of biphenyl were placed in 100 mL of the following mineral media (Gray and Thornton, 1928):

KNO_3 1.0 g/L	$FeCl_3$ 0.02 g/L
$MgSO_4$ 0.2 g/L	NaCl 0.1 g/L
$CaCl_2$ 0.1 g/L	K_2HPO_4 1.0 g/L

The distilled water used to make up this media was saturated with Aroclor 1242.

The mixture was placed in a glass-stoppered 250 mL Erlenmeyer flask that was wrapped completely with aluminum foil to keep out light and shaken at room temperature (26°C). After 1 week, 5 mL of solution was placed in a new flask containing 0.1 g of biphenyl and 100 mL of fresh media. This procedure was continued until the solution turned yellow. The yellow product, the biphenyl metabolite described by Furukawa and Matsumura (1976), indicated that biphenyl was being degraded. The solution was then transferred every 3 days to fresh media.

Three different mixed cultures were isolated in this manner. The first, the C-line, was isolated from dried Catlin soil. The second, the S-line, was isolated from soil taken from an experimental farm plot at Elwood, Illinois. Activated sludge containing PCBs from a municipal waste treatment plant at Stickney, Illinois, was applied to this plot for 7 years. The third culture, the N-line, was isolated from Hudson River sediment from the Fort Miller disposal site in New York (Leis et al., 1978). The sediment contained about 2 ppm PCBs.

PCB Degradation Studies

Originally the PCB degradation study was run on the C-line for 15, 30, and 45 days. Later studies were run on all three cultures for 5, 10, and 15 days. For these experiments, 70 mL of a 3-day old culture were added to 1400 mL of mineral media made with Aroclor 1242 saturated water. The solution was stirred rapidly. Immediately, six 100-mL aliquots were removed and placed in 250-mL Erlenmeyer flasks, with ground glass stoppers, to which 10 drops of concentrated HCl had been added. The pH of each of these control samples was about 2. Six more 100-mL aliquots were placed in Erlenmeyer flasks as the test samples. All flasks were completely covered with aluminum foil and shaken at 27°C ± 2°C. Two 80-mL aliquots of the original solution were taken, acidified, and extracted as 0-day, or 0-hour, blanks.

After a set period of time (depending upon the experiment) 2 control and 2 test flasks were removed from the shaker. Next, 10 drops of concentrated HCl were added to the test flask to stop degradation and to maintain the same pH for extraction for both the control and test samples. Eighty mL of solution from each flask were extracted with 10 mL of hexane. The solutions were extracted in a modified Erlenmeyer flask as shown in Figure 2. The solution with hexane was stirred for 10 minutes; then the flask was inverted and the layers were allowed to separate. The water layer was drained off into a beaker, and the hexane was drained into a 25-mL brown Wheaton bottle (Pierce, Rockford, IL) with a crimp top. The water was put back into the extractor and 5 mL of hexane were used to rinse out the beaker. The hexane was then poured into the extractor and the mixture was stirred for 5 minutes. The hexane was removed as before, and 5 mL of additional hexane were used to extract the solution. The Wheaton bottle containing the 20 mL of hexane was capped with an aluminum foil covering over a teflon cap and was stored until analysis. This extraction procedure was carried out for all samples.

Soil and Sludge Extractions

The soil and sludge from the experimental farm plot at Elwood, Illinois, were extracted to determine their PCB content. The sludge was a composite of sludge that had been applied to the soil about 3 months earlier. The activated sludge had been heated and anaerobically digested at a municipal waste treatment plant at Stickney, Illinois. The soil was a composite of soil from 0 to 6 inches deep and was from a plot that had received a total of 225 tons of dry solids per acre during the previous 7 years. This amounts to about eight 1-inch liquid applications per year. Applications of sludge were from June through August. The soil was tilled from 5 to 6 inches deep.

The sample soil was dried at 103°C and stored at room temperature prior to extraction. The sludge was kept refrigerated.

To extract the soil, 50 g of finely ground soil were placed in a Soxhlet extractor. About 150 mL of hexane distilled in glass were added to a 250-mL round bottom flask, and the soil was extracted for 48 hours. The hexane-cycle time was about 5 minutes. After extraction was complete, the extract was treated to remove interfering organics by adding baked florisil (450°C overnight) in increments to the round bottom flask until the solution turned colorless. The hexane was then evaporated to approximately 0.5 mL in a micro K-D evaporator and injected on the capillary column for PCB analysis.

About 150 mL of sludge were added to a modified Erlenmeyer extractor (Figure 2) along with 50 mL of hexane. This solution was stirred for about 5 minutes. The resulting solution was centrifuged (Sorvall table top centrifuge, Ivan Sorvall, Inc. Norwalk, CT) at 1,000 rpm for 5 minutes to break up the sludge-hexane emulsion. The sludge was then extracted again with 50 mL of hexane. Again the solution was centrifuged to break the emulsion. The resulting extract, colored deep yellow, was cleaned by the addition of florisil, as with the soil. The hexane then was evaporated to approximately 0.5 mL in a micro K-D evaporator and injected on the capillary column.

Sonification Study

To determine if the extraction procedure used to extract the PCBs from the test solutions could extract all the PCBs that were in the microorganisms, a 2-day degradation sample was sonified to disintegrate the microorganisms and then was extracted. This sonified sample extract was compared to an extract done as described previously.

The sonifier used was a Bronson Sonic Power (Danbury, CT) sonifier, model number S75 with an exponential horn tip. The instrument was operated at the 7 level at 6 to 7 amps for 30 minutes.

Prior to sonification, the tip and the 500-mL stainless steel beaker were rinsed with methanol and hexane. After they dried, 240 mL of a 2-day old S-line culture were placed in the beaker. The beaker was placed in an ice bath and allowed to cool for 15 minutes. Then the sample was sonified for 30 minutes. Finally, two 100-mL aliquots were acidified with 10 drops of concentrated HCl each and were extracted by the usual procedure. In addition to the sonified sample, two 100-mL aliquots of 2-day S-line culture were acidified and extracted in the normal procedure and a 2-day blank was run and extracted.

PCB VOLATILITY MEASUREMENTS

Experiments were set up to compare the changes in the volatility of PCBs between aqueous solution of PCBs and PCB solutions containing different amounts of soluble humic substances. The effect of different amounts of soil in suspension with PCB-saturated water on the volatilization of PCBs was also studied.

Humic acid standards were achieved by dissolving 100 mg and 1,000 mg of commercial humic acid (Aldrich Chemical Co., Milwaukee, WI) in 1 liter of distilled water and by adjusting the pH to 12 with NaOH pellets. The soil used in the study was the Ap horizon of an agricultural soil, Catlin silt loam. The properties of the soil are listed in Tables 1 and 2.

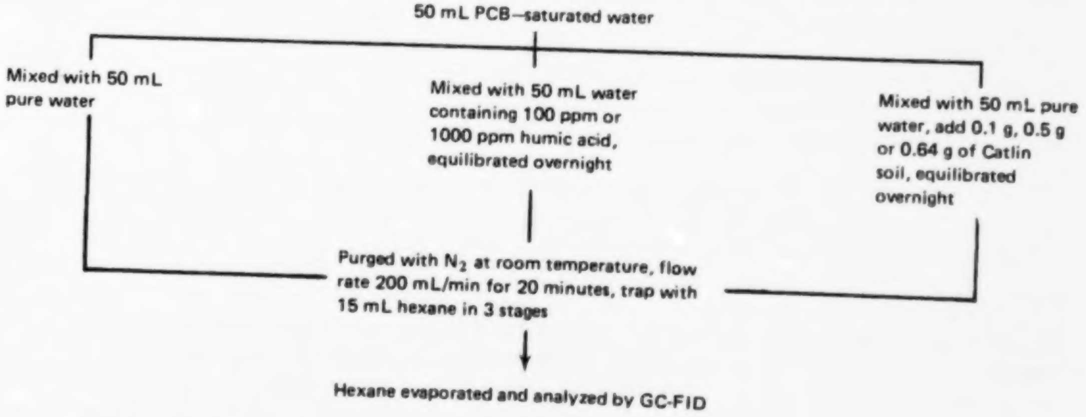
50 mL PCB—saturated water
Mixed with 50 mL pure water
Mixed with 50 mL water containing 100 ppm or 1000 ppm humic acid, equilibrated overnight
Mixed with 50 mL pure water, add 0.1 g, 0.5 g or 0.64 g of Catlin soil, equilibrated overnight
Purged with N₂ at room temperature, flow rate 200 mL/min for 20 minutes, trap with 15 mL hexane in 3 stages
Hexane evaporated and analyzed by GC-FID

Figure 5. Flow diagram of experimental protocols used to study PCB volatilization from aqueous solutions

TABLE 4. Gas chromatographic conditions used during analyses of PCBs for volatilization study.

Column: 183 cm by 2 mm in diameter glass column packed with 3 percent OV-17 on 100/120-mesh Gas Chrom Q

Carrier: He, at 40 mL/min; H_2:30 mL/min; and air:250 mL/min

Injection port: 300°C

Detector: 300°C

Temperature programmed from 170°C to 290°C at 8°/min

Attenuator: 16×10^{-12} amps/mv

The effects of humic acid and soil on volatilization of the PCBs were investigated using the experimental protocols shown in Figure 5. Triplicates of each of the samples described in Figure 5 were analyzed to obtain representative results.

PCBs dissolved in water were purged at room temperature by a stream of clean nitrogen, and the purged sample was trapped in a three-stage liquid trap filled with 5 mL of hexane in each trap (Fig. 6). The nitrogen flow rate was 200 mL/min. After 20 minutes, the hexane was pooled and evaporated in a Kuderna-Danish (KD) evaporator to 0.4 mL, then was further evaporated to dryness in a 1-mL vial by a stream of nitrogen. Five µL of hexane was then pipetted into the vial, and 1 µL of this concentrate was injected onto a gas-chromatographic column (183 cm by 2 mm I.D. glass column packed with 3 percent OV-17 on Gas Chrom Q) 100/120 mesh and was detected by a flame ionization detector (FID) on a Hewlett Packard 5830A gas chromatograph equipped with an automatic integrating recorder. The gas chromatographic conditions are given in Table 4.

The use of an electron-capture detector (ECD) was investigated earlier. The gas-purging process described was found to carry water vapor into the hexane; the concentrate when injected resulted in an erratic response from the ECD. An effort to dry the hexane layer by using salts was found to interfere with quantitation of the PCBs. Although ECD is highly sensitive to halogenated compounds and thus would normally be used for PCB analyses, FID was used in these experiments. The sensitivity of the electrometer of FID was 16×10^{-12} amps/mv, which was approaching its sensitivity limit of 1×10^{-12} amps/mv.

The GC calibration was accomplished by repeating injections of 1 µL of 500 ppm Aroclor 1242 in hexane onto the GC column and evaluating the resulting chromatograms. The area integration of the chromatograms then provided a reference for quantitation of the amounts of PCBs contained in the samples from the hexane traps.

The trapping efficiency of the volatilized PCBs in the hexane traps (Fig. 6) was evaluated by mixing 15 mL of hexane with 1 µL of 500 ppm Aroclor 1242. It was then equally distributed in the three liquid traps and stripped by using the identical purging gas-flow rate and time. The trapping efficiency was found to be 71 percent.

The purging efficiency was evaluated by adding 1 mL of acetone solution containing 0.5 μg of Aroclor 1242 to a purging flask containing 100 mL of water (Fig. 6). This solution was purged, and the contents of the hexane traps were analyzed for PCBs. The resulting chromatogram was then used to evaluate the purging efficiency.

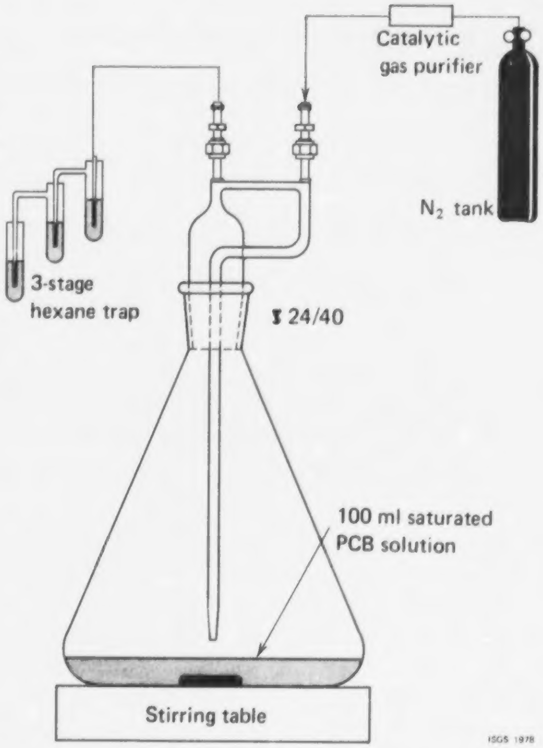

Figure 6. Purging system using 1000-mL Erlenmeyer flask

ANALYTICAL METHODOLOGY

Gas-Liquid Chromatography Instrumental Parameters

Apparatus included a Hewlett Packard (HP) model 5830A (Avondale, PA) gas chromatograph equipped with a linearized ^{63}Ni electron capture detector and an automatic integrator. A 183 cm x 2 mm I.D. glass column packed with 3 percent OV-17 on 100/120 mesh Gas Chrom. Q (Analabs Industries, North Haven, CT) was used for the analysis of samples using the perchlorination procedure. Helium served as a carrier gas at a flow rate of 60 mL/min under operating temperatures for injector, column, and detector at 300°C, 230°C, and 300°C respectively.

Samples from hexane extraction were analyzed in a 40-m wall-coated open tubular (WCOT) glass capillary column. The liquid phase, Emulphor ON-870 (Applied Science Lab., State College, PA), was custom-coated on the glass capillary columns using the techniques of Grob (1975) and Grob, Grob, and Grob (1977). The Emulphor ON-870 gave better resolution of the various isomers than other commercially available capillary-column coating materials. Helium and 5-percent methane in argon were the carrier and make-up gases, respectively, the linear velocity of the carrier gas being 45 cm/sec. The samples were split at a ratio varying from 1:90 to 1:150. The operating temperature for injector, column, and detector were 190°C, 175°C, and 320°C. All of the results were integrated and recorded on an automatic integrator.

Capillary Column Analysis

The capillary columns would sometimes become unstable with use and therefore had to be recoated several times. Varying degrees of success

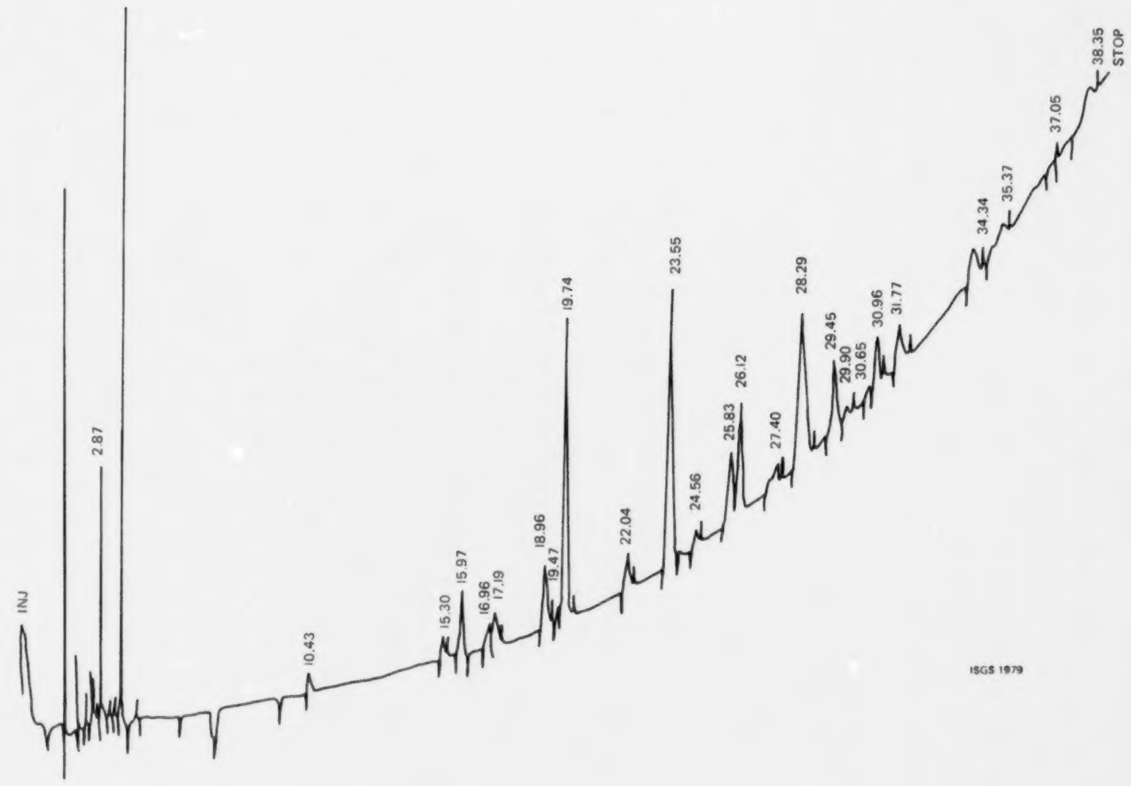

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Figure 7. Water- soluble Aroclor 1242 using a temperature-programmed column

were obtained for each recoating. As a consequence, the resolution, retention times, and column temperatures varied slightly with different columns.

For the early work on the microbial degradation using the C-line, the carrier gas was N_2 with a linear velocity of 25 cm/sec. The column was programmed from 120°C to 220°C at 20°/min. Figure 7 shows a chromatogram of water soluble Aroclor 1242 using the above column. The number of theoretical plates (N_{real}) was calculated as follows (Kaiser, 1976): $N_{real} = 5.54 \left(\frac{10\ tm}{b_{10} - b_0}\right)$ where tm = unretained retention time (solvent), and b_{10} and b_0 are the 1/2 height widths at $K = 10$ on a plot of 1/2 height widths vs. K. ($K = \frac{tr - tm}{tm}$ where tr = retention time of a certain peak). For a series of similar compounds, such as PCB isomers, N_{real} = 35,000 plates.

For the 5-, 10-, and 15-day microbial degradation studies using the C-, N-, and S-lines the conditions were as follows: the carrier gas was He with a linear velocity of 45 cm/sec. The column temperature was 192°C and the split ratio was 1:150. N_{real} = 53,000 plates. Figure 8 shows a chromatogram of water-soluble Aroclor 1242 using this column.

For the microbial degradation kinetic study using the N-line, the conditions were as follows: the carrier gas was N_2 with a linear velocity of 45 cm/sec. The column temperature was 173°C and the split ratio was 1:90. N_{real} = 33,000 plates. Figure 9 shows a chromatogram of water-soluble Aroclor 1242 using this column, which was also used in the water solubility and adsorption studies.

Prior to PCB analysis using the column described above, a mass spectrum of Aroclor 1016 was run using an Emulphor-coated WCOT capillary column. Figure 10 shows the reconstructed chromatogram. The bottom line is for mass number 188 or monochlorobiphenyl; the next line, for mass number 222 or dichlorobiphenyl; the third line, for trichlorobiphenyl; and the second to the top line, for tetrachlorobiphenyl. The top line on the figure registers the total reconstructed chromatogram.

Quantification and Identification

Samples analyzed using the capillary column were spiked with tribromobenzene as an internal standard. The quantitation measurements were carried out by obtaining the electron capture detector response factor for both the internal standard and four representative PCB isomers. The four PCB isomers used were 4-mono-; 2, 4'-di-; 2, 5, 4'-tri-; and 2, 4, 2', 4'-tetrachlorobiphenyl. The concentration of stock solution of PCB isomers were 1,502 ppm, 99.98 ppm, 60.04 ppm, and 50.17 ppm, respectively. The concentration of the stock solution of internal standard, tribromobenzene, was 24,900 ppm. A combination standard solution was prepared from these stock

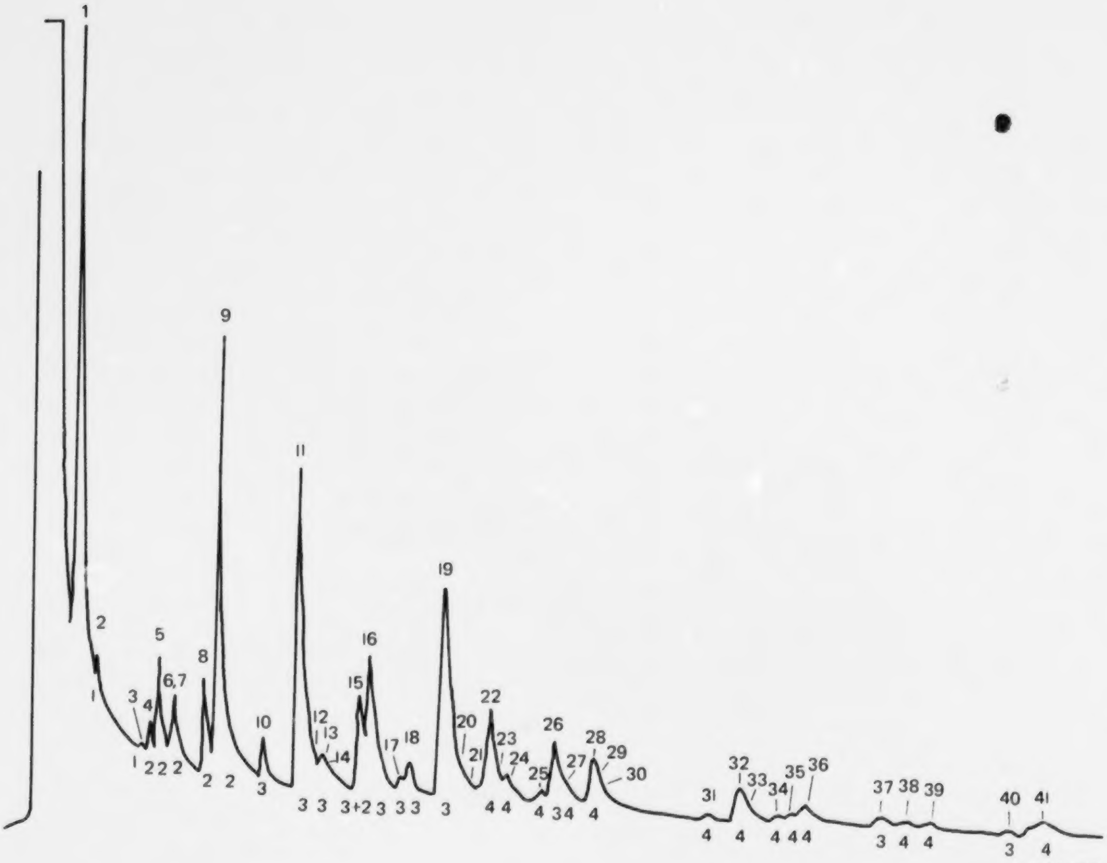

Figure 8. Water-soluble Aroclor 1242 on second capillary column. Number under peak indicates the number of chlorines on the isomer in each peak. Top number is the peak number. Peak number 1 is the internal standard.

solutions by adding 100 μL of each to 4 mL of hexane, which were subsequently condensed to approximately 0.5 mL in a micro Kuderna-Danish (K-D) concentrator. Figure 4 shows a representative chromatogram of internal standard and the four PCB isomers.

To identify each individual isomer, two approaches were adapted. (1) Seven isomers (which included the four isomers used for quantitation and the three selected isomers of known structure for additional retention-time data) were injected into the GC. By comparing the retention time of each isomer with the results from the mass spectrometer, the seven particular

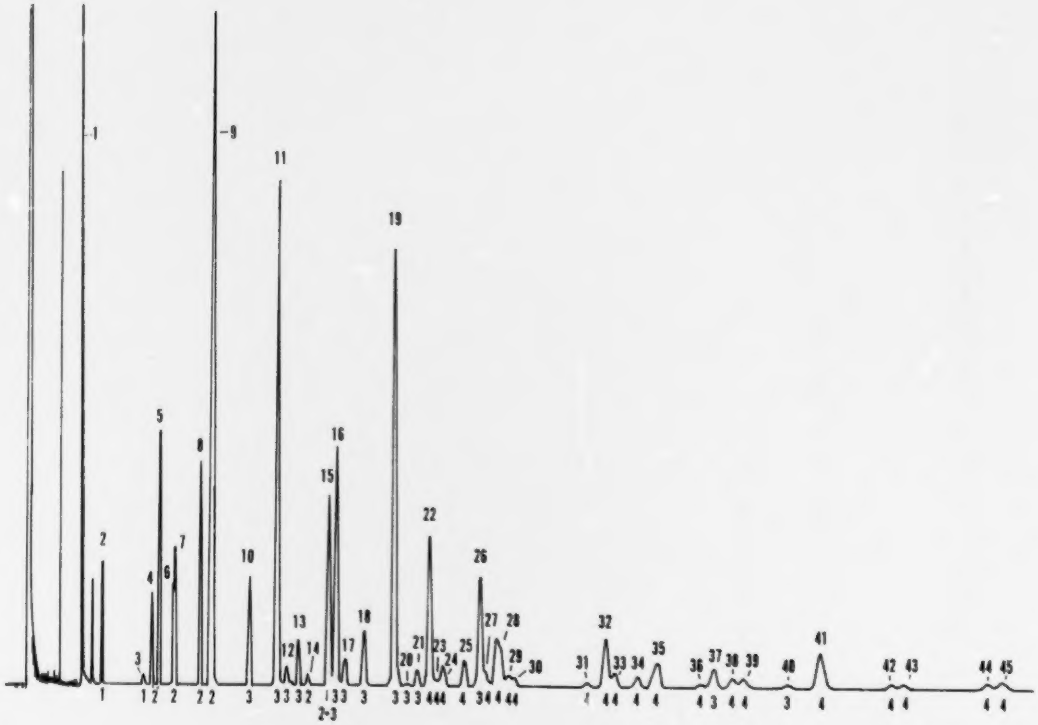

Figure 9. Water-soluble Aroclor 1242 on third capillary column

isomers could be identified. (2) By matching the relative position of the other isomers to the isomer distribution pattern reported by Sissons and Welti (1971) and Webb and McCall (1972), the major water-soluble PCB isomers were identified.

Perchlorination Procedure for Analysis of PCB

The perchlorination of PCBs to decachlorobiphenyl (Armour, 1973) was carried out in 10 mm x 150 mm hydrolysis tubes (Pierce Chemical Co., Rockford, IL), which had been modified by adding a 15 mm x 150 mm test tube to increase the volume (Fig. 11). Also, the cap of the reaction tube was modified so that the teflon insert could be easily removed for cleaning. Thorough cleaning of the insert between uses was necessary in order to prevent contamination of succeeding runs.

The teflon inserts were cleaned by boiling in a chromic acid solution for two hours (the chromic acid solution was prepared by mixing 10 to 15 mg of $K_2Cr_2O_7$ in 15 mL of water and adding sulfuric acid until the resulting

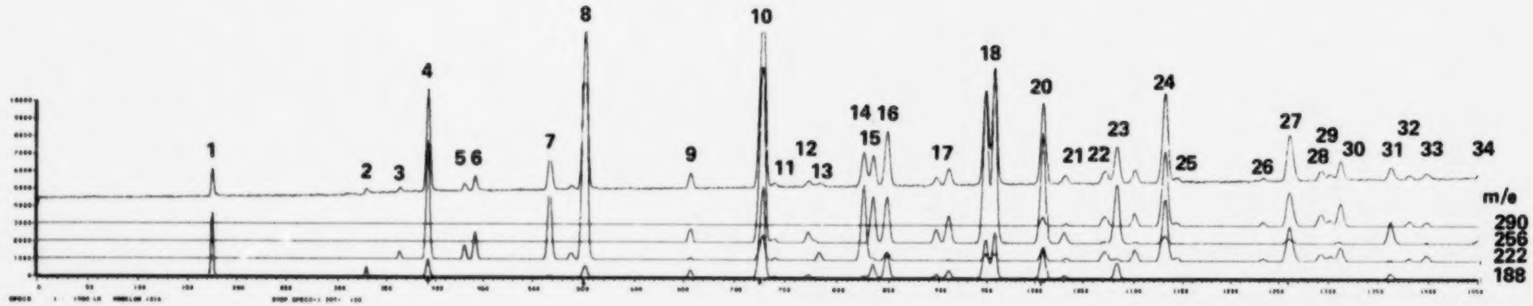

Figure 10. A reconstructed chromatogram of Aroclor 1016 obtained from mass-spectrometer

red mass dissolved). The inserts were removed from the chromic acid solution and rinsed successively with tap water, distilled water, methanol, and carbon tetrachloride.

An aliquot of a known volume of a solution of carbon tetrachloride containing PCBs was placed in a reaction vessel as described above. Antimony pentachloride (0.5 to 1.0 mL) was added to the solution. Sodium chloride crystals were added as a boiling aid. The reaction vessels were capped securely to prevent losses of PCBs by volatilization. The reaction was carried out at 200°C ± 5°C for 16 hours. Preliminary studies had shown that 16 hours at 200°C were sufficient for complete perchlorination of the sample.

The reaction vessel was allowed to cool and the caps were loosened. Then 4 to 5 drops of 6N HCl were added slowly (due to the violent reaction). To quench the reaction and to prevent precipitation of antimony oxychloride (Berg, Diosady, and Rees, 1972), 1 mL of HCl was added. To ensure that the HCl was well mixed, the caps were closed tightly and the vessels were shaken for about 10 seconds. The caps were then opened and 1.0 mL of Mirex (perchloropentacyclodecane, Alfred Bader Library of Rare Chemicals, a Division of Aldrich, Inc., Milwaukee, WI) was added (at a concentration of 500 ppb in a solution with benzene), followed by an additional 3 mL of benzene. The caps were again closed tightly and the vessels shaken vigorously for 1 minute. To remove any impurities and/or moisture (Armour, 1973), the upper benzene layer was removed with a long-nosed transfer pipette to test tubes containing Na_2SO_4 and $NaHCO_3$. The benzene solution was transfered from the test tube to a K-D evaporator, and NaCl crystals were added as a boiling aid. The sample was then condensed to 0.4 mL in a 100°C ± 0.5°C water bath. About 4 mL of benzene were added and condensation to 0.4 mL was repeated a second time. The addition of 4 mL of benzene and condensation to 0.4 mL were repeated for a third and final time. Then 4 mL of hexane were added to aid in the GC analysis. A block diagram of the procedure is shown in Figure 12. Analysis of standard Aroclor 1242 solutions yielded a factor of 0.737 for conversion of decachlorobiphenyl (DCB) concentrations to Aroclor 1242 concentrations. Therefore, all DCB concentrations obtained from the perchlorinated samples were multiplied by 0.737 for conversion to Aroclor 1242 concentration. The GC instrumental parameters given previously were used for the analysis.

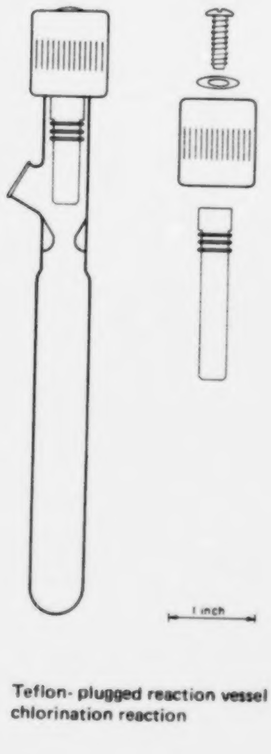

Figure 11. Teflon-plugged reaction vessel used in perchlorination reaction

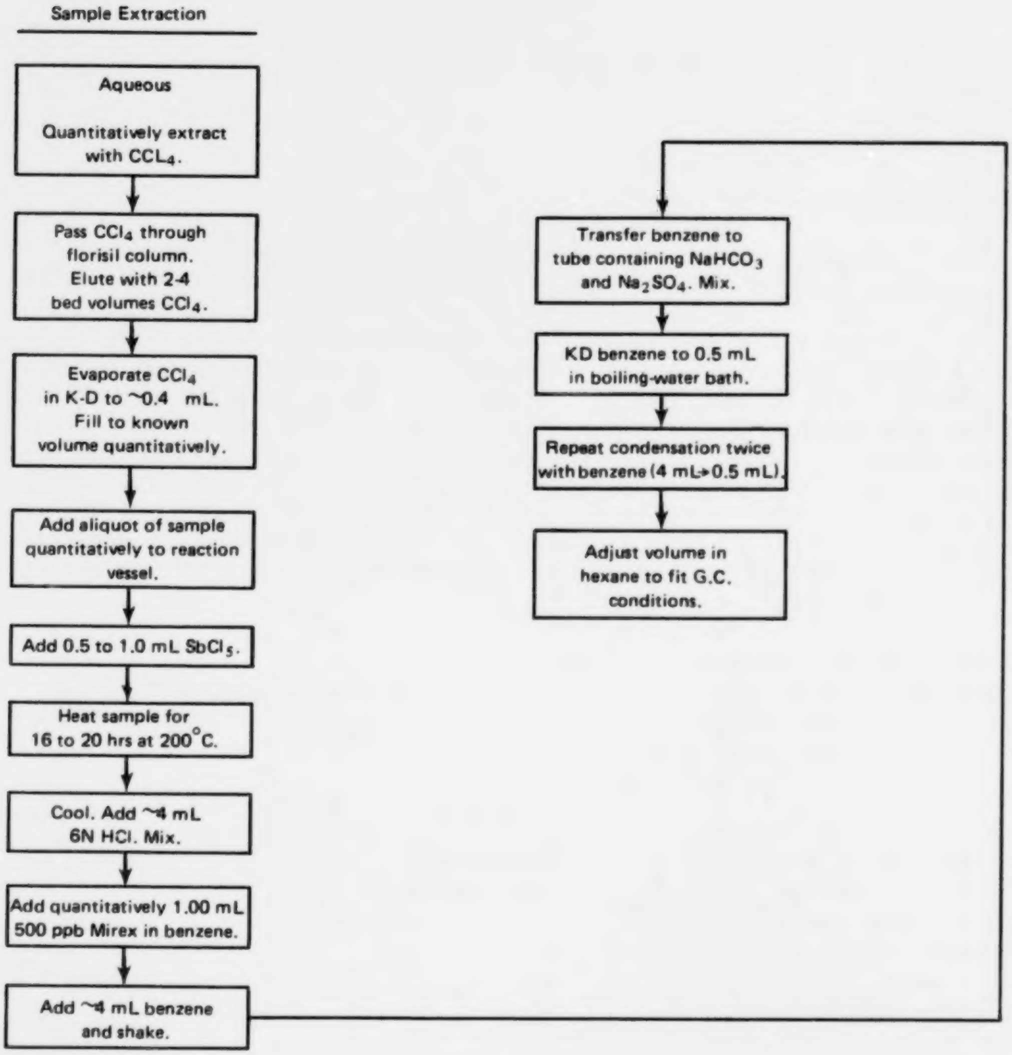
Sample Extraction
Aqueous
Quantitatively extract with CCL_4.
Pass CCl_4 through florisil column. Elute with 2-4 bed volumes CCl_4.
Evaporate CCl_4 in K-D to ~0.4 mL. Fill to known volume quantitatively.
Add aliquot of sample quantitatively to reaction vessel.
Add 0.5 to 1.0 mL $SbCl_5$.
Heat sample for 16 to 20 hrs at 200°C.
Cool. Add ~4 mL 6N HCl. Mix.
Add quantitatively 1.00 mL 500 ppb Mirex in benzene.
Add ~4 mL benzene and shake.
Transfer benzene to tube containing $NaHCO_3$ and Na_2SO_4. Mix.
KD benzene to 0.5 mL in boiling-water bath.
Repeat condensation twice with benzene (4 mL→0.5 mL).
Adjust volume in hexane to fit G.C. conditions.

Figure 12. Schematic block diagram of the perchlorination procedure for the analysis of PCB from aqueous and solid samples.

SECTION 5

SOLUBILITY OF PCBs IN WATER[1]

RESULTS AND DISCUSSION

Quantitation and Identification

A PCB mixture contains a variety of isomers. Sissons and Welti (1971) have reported that for Aroclor 1242, 1254, and 1260, the possible number of isomers were 45, 69, and 78. Because it was not possible to obtain all the individual isomers for quantitation and identification of the PCBs analyzed in this study, only four isomers were used for quantitation. An assumption was made that all of the mono-chlorobiphenyl isomers gave the same electron capture detector response and likewise, the di-, tri-, and tetra-chlorobiphenyls. Table 5 lists the relative response of an electron capture detector (^{63}Ni) to the internal standard and several PCB isomers. Although the responses of the electron capture detector to each isomer are not exactly the same, they are in the same range. The isomers with five or more chlorine substitutions were quantified by the response of the electron capture detector to tetrachlorobiphenyl (2, 4, 2', 4'-).

To confirm the above assumption for quantitative analysis, two standard solutions were checked. A standard containing 40.6 mg of Aroclor 1242 in 10 mL of hexane solution was prepared. A 10-μL volume of solution and 100 μL of internal standard (tribromobenzene) were injected into 4 mL of hexane, and then evaporated in a micro K-D condenser to approximately 0.5 mL. Three μL of the concentrate were injected into

TABLE 5. The relative response of a ^{63}Ni electron capture detector to tribromobenzene and several PCB isomers.

Chemical	Relative response (μg/area)
Internal standard (tribromobenzene)	5.3234×10^{-5}
4	3.3772×10^{-3}
2,4'	2.2853×10^{-4}
2,5,2'	1.9866×10^{-4}
2,5,4'	1.0879×10^{-4}
2,4,2',5'	9.6283×10^{-5}
2,4,2',4'	9.0012×10^{-5}
2,3,2',5'	

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[1] Authors: M. C. Lee, E.S.K. Chian, and R.A. Griffin

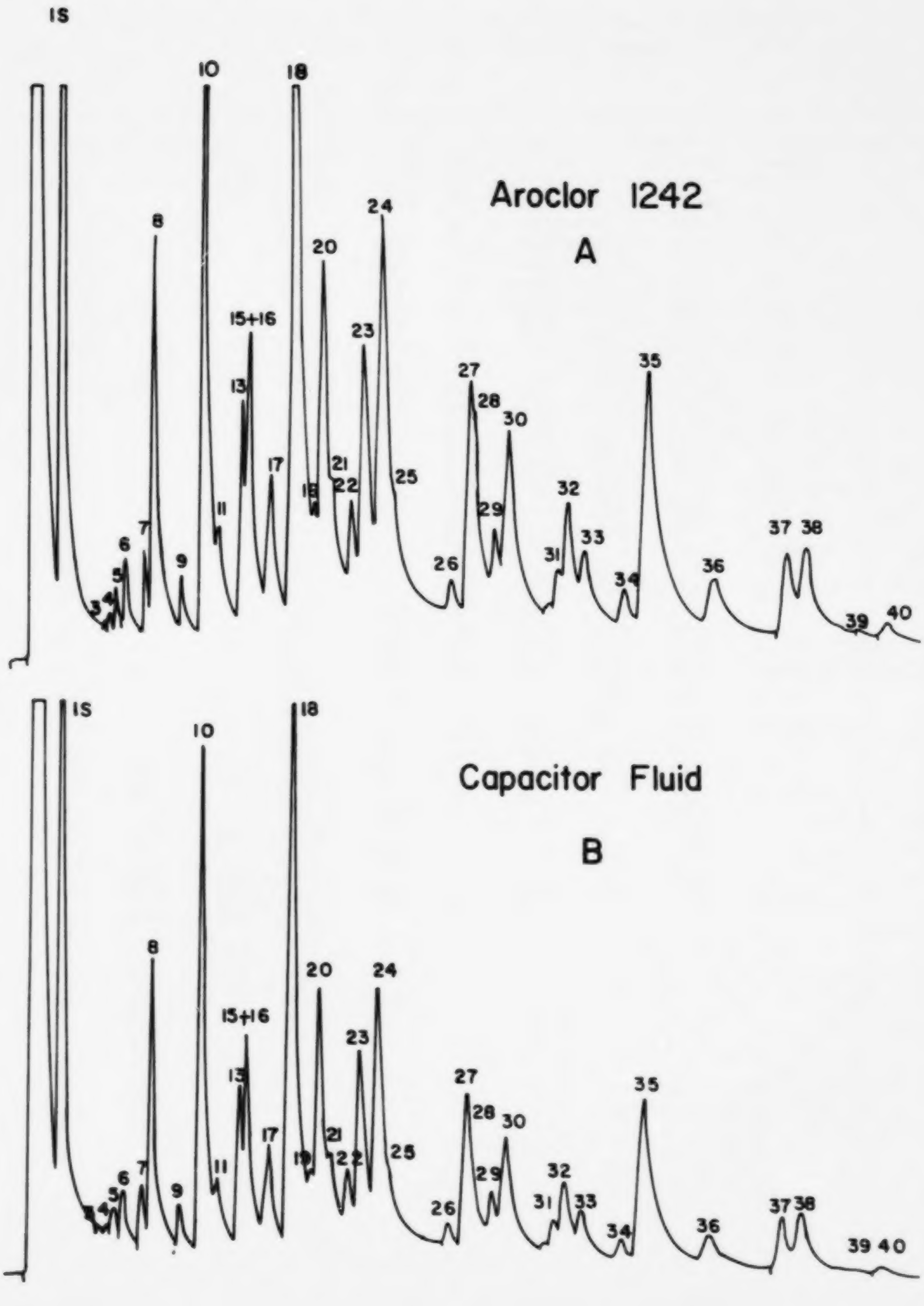


Figure 13. A comparison of hexane-soluble Aroclor 1242 and used capacitor fluid: (A) Aroclor 1242, (B) used capacitor fluid

TABLE 6. The quantitative composition and percentage of contribution of the individual water-soluble isomers in Aroclors and capacitor fluid.

Peak no.	No. of Cl	Identi-fication	AR 1016[a] (μg L^{-1})	AR 1016[a] (%)	AR 1221[a] (μg L^{-1})	AR 1221[a] (%)	AR 1242[b] (μg L^{-1})	AR 1242[b] (%)	AR 1254[b] (μg L^{-1})	AR 1254[b] (%)	Capacitor fluid[a] (μg L^{-1})	Capacitor fluid[a] (%)
1	1	2	84.78	9.36	2572.28	73.15	121.59	17.30			113.87	16.31
2	1	3	13.31	1.47	45.75	1.30						
3	1	4	12.74	1.47	622.64	17.71	15.07	2.14			14.81	2.12
4	2		19.71	2.18	13.48	0.38	9.06	1.29			8.07	1.16
5	2	2,2′	18.80	2.08	23.50	0.67	21.18	3.01			24.65	3.52
6	2	2.4	25.94	2.86	25.57	1.50	23.76	3.38			23.72	3.40
7	2	2,3′	38.62	4.26	33.70	0.96	30.60	4.35			27.20	3.90
8	2	2,4′	171.78	18.97	109.59	3.12	138.93	19.77			122.42	17.53
9	3	2,6,2′	10.29	1.14			8.33	1.19			8.52	1.22
10	3	2,5,2′	87.03	9.61	5.26	0.15	61.35	8.73	0.37	0.53	59.19	8.48
11	3		2.72	0.30	1.27	0.04	2.15	0.31			1.91	0.27
12	3				1.87	0.05	0.48	0.07			0.41	0.06
13	3	2,4,2′	5.78	0.64	0.71	0.02	4.50	0.64			4.93	0.71
14	2	3,4′	4.77	0.53	4.13	0.12	2.98	0.42			2.99	0.43
15	2&3	4,4′;2,3,2′	49.38	5.45	9.07	0.26	35.30	5.02			33.66	4.82
16	3	2,4,3′	33.52	3.70	1.94	0.06	27.47	3.91			27.05	3.87
17	3	2,4,4′	16.62	1.84	1.71	0.05	9.87	1.40			11.03	1.58
18	3	2,5,4′	110.76	12.23	4.73	0.13	65.07	9.26	1.09	1.56	67.26	9.63
19	3	3,4,2′	5.43	0.60	0.74	0.02	2.59	0.37	0.28	0.40	2.86	0.41
20	4	2,5,2′,5′	35.87	3.96	1.66	0.05	22.25	3.17			25.09	3.59
21	4		5.48	0.61	0.64	0.02	3.59	0.51			4.10	0.59
22	4		6.95	0.77	0.78	0.02	4.09	0.58			4.95	0.71
23	3&4	2,4,2′,5′	31.83	3.51	1.32	0.04	19.51	2.78			23.75	3.40
24	4	2,4,2′,4′	27.34	3.02	1.08	0.03	15.88	2.26	4.57	6.54	14.04	2.01
25	4		9.18	1.01			3.37	0.48			2.58	0.37
26	4		2.39	0.26			1.09	0.16			1.47	0.21
27	4	2,3,2′,5′	19.77	2.18	3.61	0.10	12.83	1.83	2.87	4.11	10.92	1.56
28	4		8.16	0.90	0.37	0.01	3.13	0.45			3.83	0.55
29	4		5.26	0.58			2.50	0.36	0.23	0.33	3.37	0.48
30	4	2,5,3′,4′	14.91	1.65	1.48	0.04	7.21	1.03	1.09	1.56	9.08	0.13
31	3		5.27	0.58			4.70	0.67			6.45	0.92
32	4		3.03	0.33			2.70	0.39	2.85	4.08	4.23	0.61
33	4		2.12	0.23			2.63	0.38			3.33	0.48
34	3		1.85	0.20			0.82	0.12	2.33	3.34	1.29	0.18
35	4	2,4,3′,4′	14.16	1.56	0.45	0.01	9.79	1.39	14.25	20.40	14.91	2.14
36	5								0.55	0.79		
37	5						0.99	0.14			1.54	0.22
38	5								6.46	9.25		
39	5						2.47	0.35	3.07	4.40	4.22	0.60
40	5						2.84	0.40	2.67	3.82	4.63	0.66
41									0.29	0.42		
42									1.78	2.55		
43	5								2.24	3.21		
44	5								1.72	2.46		
45	5								6.20	8.88		
46									0.47	0.67		
47												
48									1.48	2.12		
49	6								4.46	6.39		
50									0.97	1.39		
51									0.80	1.15		
52									5.19	7.43		
53									1.56	2.23		
Total			905.55		3516.33		702.67		69.84		698.33	

[a] Indicates duplicated samples.
[b] Indicates triplicated samples.

the gas-liquid chromatograph. A second standard solution containing capacitor fluid was prepared by adding 28 mg of capacitor fluid to 10 mL of hexane. The same procedure as with the Aroclor 1242 standard was repeated. The results of the analysis showed that 42.77 mg of Aroclor 1242 were quantified as compared to 40.60 mg of Aroclor 1242 actually present in the sample; the percentage of error was 5.34 percent. Versus 28 mg of capacitor fluid added to the sample, 30.57 mg of capacitor fluid were determined; the percentage of error was 9.18 percent. In both cases, the error was less than 10 percent. The results show that, considering the errors normally associated with PCB analyses, the quantitative method developed in this study gave satisfactory results. By using an internal standard and four PCB isomers, the determinations of concentrations of individual PCB isomers in a mixture of isomers were relatively accurate.

GC chromatograms of both hexane-soluble Aroclor 1242 and capacitor fluid are shown in Figure 13; both have the same isomer distribution pattern. This indicates that the Aroclor 1242 that was originally impregnated into the capacitor had not undergone any significant changes during 10 years of use or during the "burn out" of the capacitor.

The identification of the water-soluble fractions of several Aroclors and capacitor fluid are shown in Table 6. Webb and McCall (1972) have also reported data on isomer distributions; peak 3 (4-mono-chlorobiphenyl) was not reported by them for Aroclor 1242; and peak 10 (2,5,2'-tri-chlorobiphenyl), peak 18 (2,5,4'-tri-chlorobiphenyl), and peak 19 (3,4,2'-tri-chlorobiphenyl), were not reported for Aroclor 1254. In addition, peak 22 and peak 23 (a combination of a tri-chlorobiphenyl and 2,4,2', 5'-tetra-chlorobiphenyl) were reported by Webb and McCall (1972) but were not found in Aroclor 1254 in this study. The explanation for this apparent discrepancy seems to be in the higher resolution of the Emulphor-coated capillary column used in this study, differences in quantitation techniques, and/or possibly differences in batches of Aroclors (EHRC, 1976; Lloyd et al., 1976).

The Time Dependence of PCB Dissolution in Water

One of the major difficulties in determining the aqueous solubility of Aroclors is the length of time necessary to reach a state of equilibrium between the Aroclors and water. Figure 14 shows that about 5 months were required to reach a saturation point for both Aroclor 1242 and capacitor fluid. Haque, Schmedding, and Freed (1974) reported that the equilibration of Aroclor 1254 in water occurred in about 2 months. During the initial solubilization of about one week (Table 7), the percentages of tri- and tetra-chlorobiphenyl were high (about 61 percent and 32 percent, respectively); however, after the solution approached equilibrium, the percentages changed. The values for mono-, di-, tri-, and tetra-chlorobiphenyl became 20 percent, 35 percent, 31 percent, and 15 percent, respectively. That is, the composition of water-soluble Aroclor 1242 changed during the solubilization process and was also no longer the same as that of the original Aroclor 1242 fluid. Higher portions of low-chlorinated isomers predominated in the water-soluble Aroclor 1242.

A comparison of the solubility of PCB isomers in Aroclor 1242 to the individual isomers (Table 8) clearly indicates that the solubility of individual isomers was lower in the Aroclor mixture than when measured alone. It also appeared that the presence of other chlorinated isomers impaired the dissolution of the lower-chlorinated isomers in the mixture, but, on the contrary, the dissolution of the higher chlorinated isomers did not seem to be affected as greatly by the presence of lower chlorinated isomers.

Table 9 shows quantitative values of the water solubility of the individual isomers with respect to time. The isomers represented by peaks 8, 10, 17, 18, 20, and 24 dissolved rapidly in the water. The results shown for Aroclor 1242 also apply to capacitor fluid.

Solubility of Aroclors and Capacitor Fluid

Representative GC chromatograms of the water-soluble PCBs, that is, Aroclor 1016, 1221, 1242, and 1254, and capacitor fluid used in this study, are shown in Figure 15. The quantitative composition and percentages of contribution of the individual isomers (Table 6) show that in Aroclor 1016 peak numbers 1, 8, 18, and 20 were the major peaks of mono-, di-, tri-, and tetra-chlorobiphenyl. They represented 76, 56, 35, and 21 percent of the individual peaks, respectively. In Aroclor 1221 the four major peaks

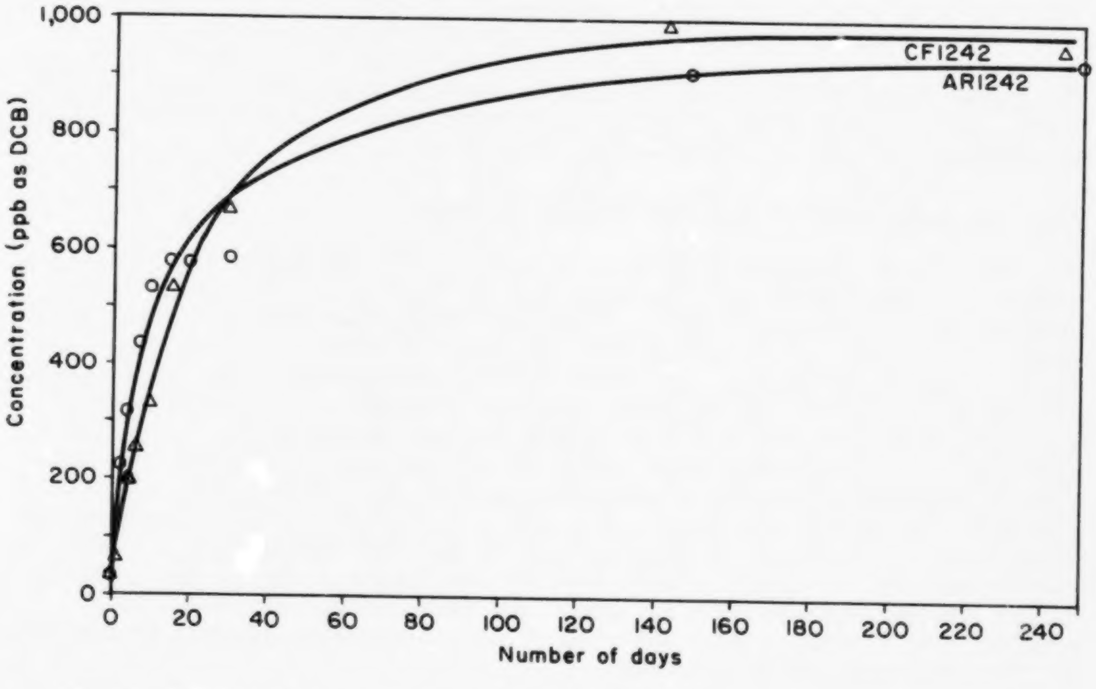


Figure 14. The solubility of Aroclor (AR) 1242 and used capacitor fluid (CF) 1242 in water as a function of time

TABLE 7. The percentage of PCB isomers in water-soluble Aroclor 1242.

	Number of days						
Number of Cl	7 (%)	20 (%)	30 (%)	50 (%)	149 (%)	251 (%)	Hexane-soluble (%)
1	-[a]	-[a]	-[a]	-[a]	20	20	-[a]
2	6	29	44	45	34	35	12
3	61	58	47	45	31	31	46
4	32	13	9	11	17	15	42

[a] No data available because of poor resolution between IS and monochlorinated biphenyl.

of mono-, di-, tri-, and tetra-chlorobiphenyl were represented by peak numbers 1, 8, 10, and 27, and the corresponding percentages were 79, 45, 22, and 34 percent. In Aroclor 1242, peak numbers 1, 8, 18, and 20 were the major peaks of mono-, di-, tri-, and tetra-chlorobiphenyl. The percentages of these peaks were 89, 57, 30, and 22 percent, respectively. In Aroclor 1254 the major peaks of tri-, tetra-, and penta-chlorobiphenyls were represented by peaks numbered 34, 35, and 45; the respective percentages were 57, 55, and 27 percent. In capacitor fluid, the four major peaks were represented by peak numbers 1, 8, 18, and 20 for mono-, di-, tri-, and tetra-chlorobiphenyls, respectively; the respective percentages were 88, 54, 31, and 22 percent.

The overall compositions of mono-, di-, tri-, tetra-, penta-, and hepta-chlorobiphenyl isomers in the water-soluble fraction of these Aroclors and capacitor fluid are listed in Table 10. In comparing the composition of the water-soluble Aroclors to the original Aroclors, such as reported by Thurston (1971) and measured in this study, the water-soluble PCBs were found to be richer in the lower-chlorinated isomers than were the original PCBs. Aroclor 1254 is reported to contain isomers from tetra- to hepta-chlorobiphenyl in the original fluid. The GC traces of hexane-soluble Aroclor 1254 (for example, Stalling and Huckins, 1971, and Sissons and Welti, 1971)

TABLE 8. A comparison of the aqueous solubility of some PCB isomers contained in Aroclor 1242 to the pure individual isomers.

	Solubility	
Isomer	In mixture ($\mu g\ L^{-1}$)	Individual ($\mu g\ L^{-1}$)
4	15.07	400[a]
2,2′	21.18	900[a]
2,4′	138.93	637[b]
2,5,2′	61.35	248[b]
2,5,2′,5′	22.25	26.5[b]

[a] Reported by Hoover (1971).

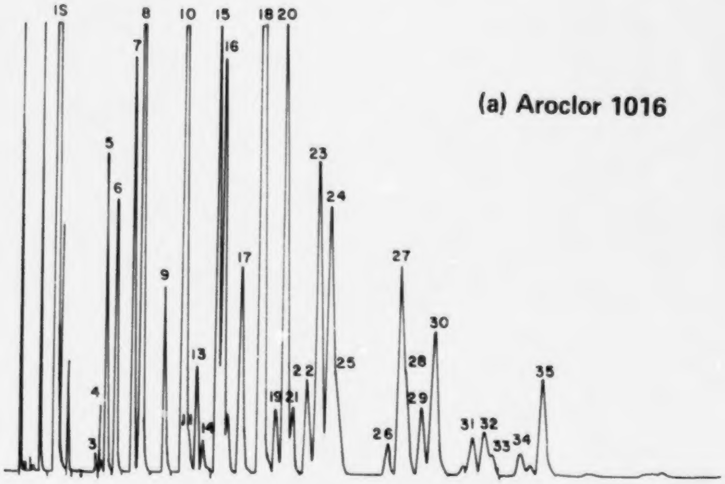
[b] Reported by Haque and Schmedding (1975).

show some small peaks in the position of trichlorobiphenyl, as has also been confirmed in this study. The trichlorobiphenyls are peaks 10, 18, and 19, shown in Figure 15e. Because trichlorobiphenyls are more water soluble than the more highly chlorinated biphenyls, detection of trace amounts in water is reasonable. The hexa- and hepta-chlorobiphenyls are enriched in the Aroclor 1254 fluid and do not dissolve readily in water. The low solubility of these highly chlorinated isomers in water is apparently the reason for this situation.

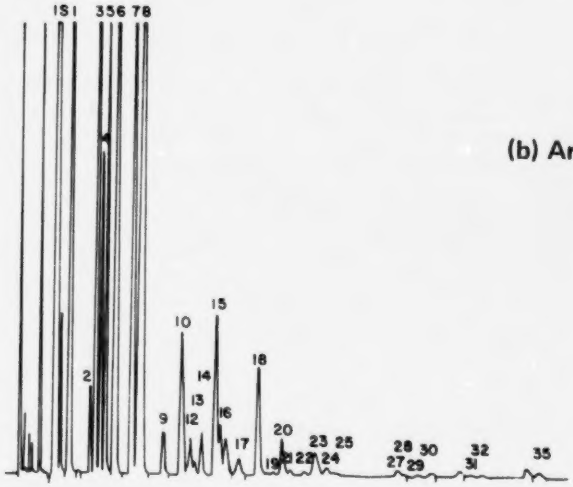
TABLE 9. A quantitative comparison of water-soluble isomers in Aroclor 1242 with respect to time

Peak No.	No. of Cl	Identification	Concentration					
			7 days ($\mu g\ L^{-1}$)	20 days ($\mu g\ L^{-1}$)	30 days ($\mu g\ L^{-1}$)	50 days ($\mu g\ L^{-1}$)	149 days ($\mu g\ L^{-1}$)	251 days ($\mu g\ L^{-1}$)
1	1	2						
2	1	3					124.60	121.59
3	1	4						
4	2						7.50	15.07
5	2	2,2′			1.00	1.69	5.83	9.06
6	2				3.18	1.78	20.80	21.18
7	2	2,3′				2.93	23.24	23.76
8	2	2,4′	2.90	27.30	9.10	14.07	19.63	30.60
9	3	2,6,2′			71.18	78.45	141.85	138.93
10	3	2,5,2′	5.52	22.97	1.40	1.72	8.13	8.33
11	3				41.05	41.20	62.48	61.35
12	3	2,4,2′						2.15
13	3			-				0.48
14	2	3,4′			-	1.71	10.00	4.50
15	2&3	4,4′;2,3,2′	-	8.83				2.98
16	3	2,4,3′			16.25	17.19	26.15	35.30
17	3	2,4,4′	2.55	-			29.83	27.47
18	3	2,5,4′	20.22	35.15	4.08	4.63	9.83	9.87
19	3	3,4,2′			43.28	48.20	63.76	65.07
20	4	2,5,2′,5′	1.58	6.67			2.59	2.59
21	4				8.94	8.78	24.05	22.25
22	4					0.64	2.66	3.59
23	3&4	2,4,2′,5′			0.55	0.49	3.78	4.09
24	4	2,4,2′,4′	11.12	7.39		2.11	17.95	19.51
25	4				8.93	9.12	19.85	15.88
26	4						4.15	3.37
27	4	2,3,2′,5′					1.11	1.09
28	4					0.69	12.75	12.83
29	4					0.74	4.10	3.13
30	4	2,5,3′,4′				1.42		2.50
31	3						9.15	7.21
32	4					0.59	4.53	4.70
33	4						4.10	2.70
34	3						5.43	2.63
35	4	2,4,3′,4′	1.96				0.73	0.82
36	5					2.18	13.83	11.62
37	5							
38	5						2.53	0.99
39	5		0.71					
40	5						4.79	2.47
Total			46.56	108.31	208.94	240.33	671.86	2.84 702.67

(-) Indicates peaks too small to quantify.

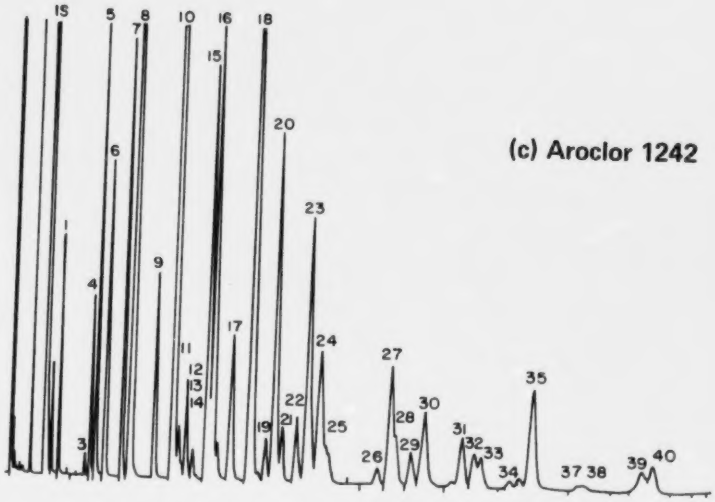


(a) Aroclor 1016

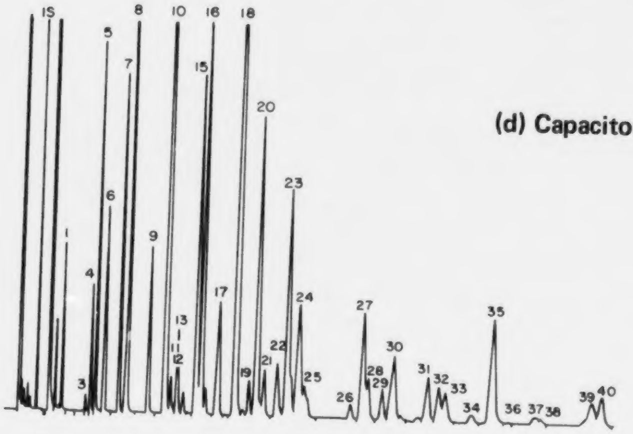


(b) Aroclor 1221

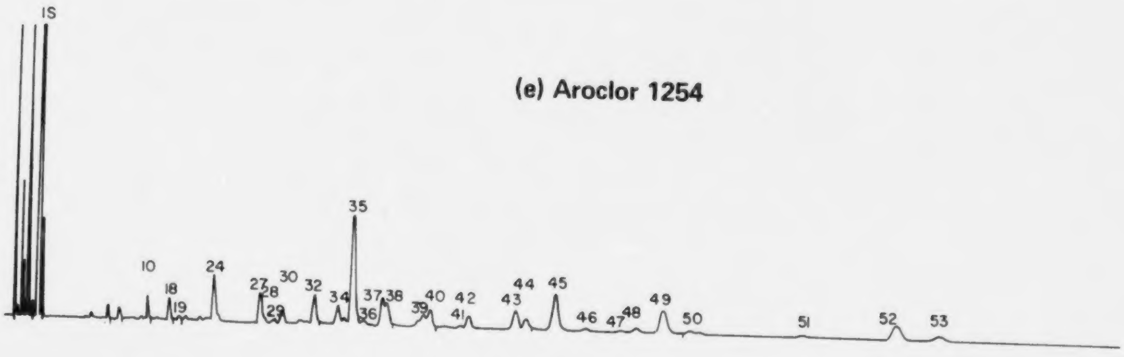
Figure 15. GC chromatograms of water-soluble Aroclors and used capacitor fluid.



(c) Aroclor 1242



(d) Capacitor Fluid



(e) Aroclor 1254

Figure 15. *Continued*

The comparison of Aroclor 1242 and capacitor fluid as shown in Figure 15c and d indicated that the distribution of isomers was identical, but actually the composition was slightly different (Tables 6 and 10). The concentrations of mono-, and di-chlorobiphenyl were slightly higher in capacitor fluid; however, each batch of Aroclor may differ slightly in isomer composition. On this basis, the Aroclor 1242 and capacitor fluid were considered to be essentially identical. Aroclor 1016 has a composition similar to Aroclor 1242 except for isomers with 5 or more chlorines. The distribution of isomers in water-soluble Aroclor 1016 and Aroclor 1242 indicated that peaks 37 to 40 (pentachlorobiphenyls) were absent in the chromatogram of Aroclor 1016 (Figure 15a and c). This observation was consistent with the original compositions of Aroclor 1016 and 1242. Aroclor 1221 (21 percent chlorine content) and Aroclor 1254 (54 percent chlorine content) were different in their isomer distribution patterns in water, as shown in Figure 15b and e. The lower-chlorinated isomers were predominant in Aroclor 1221, whereas higher-chlorinated isomers were predominant in Aroclor 1254.

The solubility of the PCBs and capacitor fluid in water is summarized in Table 11. It should be noted that the data of MacKay and Wolkoff (1973) were calculated values and that the solubility of Aroclor 1016 reported by Tucker, Litschgi, and Mees (1975) was estimated from the solubility of Aroclor 1242 on the assumption that Aroclor 1016 contained more of the lower-chlorinated isomers than did Aroclor 1242. The aqueous solubility of Aroclors 1016, 1242, and 1254 measured in this study was higher than those reported in the literature. The discrepancy in the solubility data for Aroclor 1254 may be attributed to the quantitation method employed in this study. The response of the electron capture detector to tetrachlorobiphenyl was used to estimate the values of the water-soluble fractions of Aroclor 1254, which consisted of a high proportion of tetra- and penta-chlorobiphenyls. The response factor used for the penta-isomers may have yielded a high value for the overall solubility of Aroclor 1254.

TABLE 10. Summary of isomer composition of water-soluble Aroclors and capacitor fluid.

Number of Cl	AR 1221 (%)	AR 1016 (%)	AR 1242 (%)	Capacitor fluid (%)	AR 1254 (%)
1	92	12	19	18	0
2	7	34	35	32	0
3	1	35	31	36	20
4	-[a]	19	14	13	56
5	0	0	1	1	24
6	0	0	0	0	-
7	0	0	0	0	-

[a] (-) indicates trace amount.

TABLE 11. A summary of the solubility of PCBs and capacitor fluid in water.

AR 1016 (μg L^{-1})	AR 1221 (mg L^{-1})	AR 1242 (μg L^{-1})	AR 1248 (μg L^{-1})	AR 1254 (μg L^{-1})	AR 1260 (μg L^{-1})	Capacitor fluid (μg L^{-1})	Temperature (°C)	Authors
906	3.5	703		~70		698	room (23 ± 2°C)	This study (1978)
420 ± 80		340 ± 60					room (25 ± 1°C)	Paris et al. (1978)
				45 ± 10			room	Lawrence & Tosine (1976)
220-250		200					room	Tucker et al. (1975)
				~56			room	Haque et al. (1974)
		240	54	12	2.7		25°C	Mackay & Wolkoff (1973)
		200	100	50	~25		20°C	Nisbet & Sarofin (1972)
				43 41			26°C 4°C	Nelson (1972)
	5.0 mg L^{-1} in fresh water 3.8 mg L^{-1} in salt water			0.3-3 mg L^{-1} in fresh water 0.3-1.5 mg L^{-1} in salt water			room	Zitko (1970, 1971)

The solubility of Aroclor 1016 and 1242 reported in this study also appears to be higher than that reported by other investigators. This appears to be due to differences in experimental and quantitation methods and possibly is due to differences in "batches" of Aroclors. A possible explanation for the lower values reported by earlier workers (Nisbet and Sarofin, 1972; MacKay and Wolkoff, 1973; and Paris, Steen, and Baughman, 1978) may be a result of the lack of information on the periods of time needed to reach equilibrium in water. This study shows that 5 months were necessary for Aroclor 1242 to reach equilibrium in aqueous solution, and Haque, Schmedding, and Freed (1974) have shown that 2 months were necessary for Aroclor 1254. Whereas, Paris, Steen, and Baughman (1978) reported that saturation of Aroclor 1016 and 1242 in water occurred in less than 1 week. The solubility of Aroclor 1221 obtained in this study was close to that reported by Zitko (1970). Because the solubilities of capacitor fluid have not been reported previously, no comparison can be made. Therefore, caution should be used when interpreting solubility data reported for Aroclors; the effect of the time-dependence of the solubilization should be considered.

SECTION 6

ADSORPTION OF WATER SOLUBLE PCBs BY SOIL MATERIALS AND COAL CHARS[1]

RESULTS AND DISCUSSION

The data for PCB adsorption by the various earth materials used in this study are shown in Figure 16 as the amount of PCB adsorbed in relation to the equilibrium PCB concentration. Similar results for the low-temperature ashed samples are shown in Figure 17.

Several results are evident from the data presented in Figures 16 and 17. The first result was that, over the concentration range studied, PCB adsorption by all the earth materials could be described by the linear relationship:

$$x/m = KC, \qquad (1)$$

where x/m = the amount of PCB adsorbed per unit weight of adsorbent (μg/g),
K = an adsorption constant (mL/g),
and C = the equilibrium PCB concentration (μg/mL).

The PCB adsorption constant (K) for each adsorbent was obtained from the slope of the line and is shown in Figure 16 and 17. The Freundlich adsorption constant (K_F) can be obtained from the following relation:

$$x/m = K_F C^n,$$

where K_F(μg/g) and n (mL/g) are constants and the x/m and C are as defined in equation (1). It is evident that the PCB adsorption data reported here are a special case of the Freundlich equation where $n = 1$. For the case $n = 1$, K_F and K are identical, thus K_F values reported in the literature for other compounds in units of μg/g can be compared directly with the K values reported here.

Another view of the PCB adsorption constant (K) is as a partition coefficient. The parameter K is the ratio of the solid phase PCB (x/m) to the solution phase PCB (C). That is, the constant K is the partition coefficient between adsorbed and solution phases of PCB in the experimental system used in this study. In either view, a simple linear relation (equation [1]) described the adsorption of PCB from aqueous solution and yielded an adsorp-

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[1] Authors: M. C. Lee, R. A. Griffin, M. L. Miller, and E.S.K. Chian

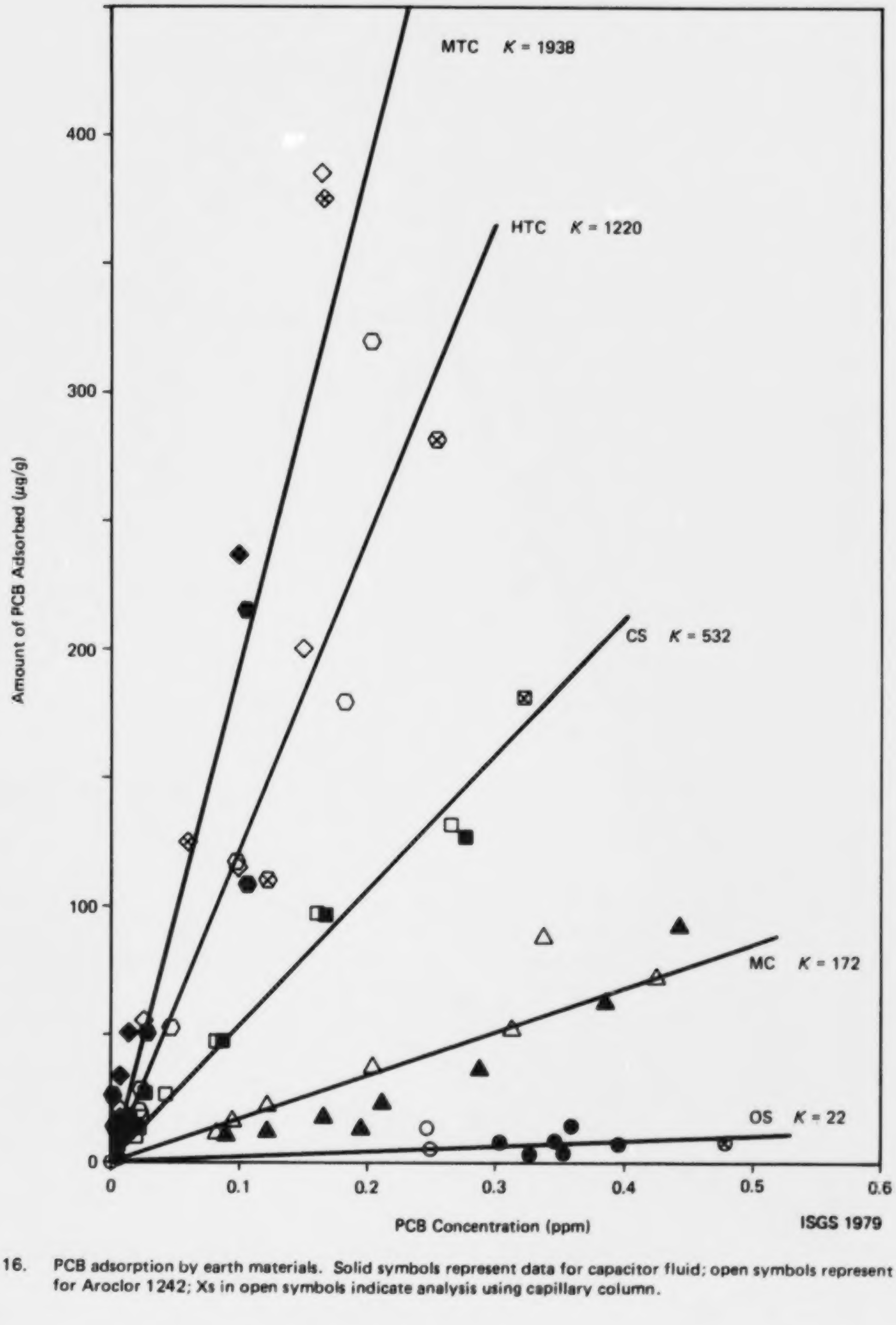

Figure 16. PCB adsorption by earth materials. Solid symbols represent data for capacitor fluid; open symbols represent data for Aroclor 1242; Xs in open symbols indicate analysis using capillary column.

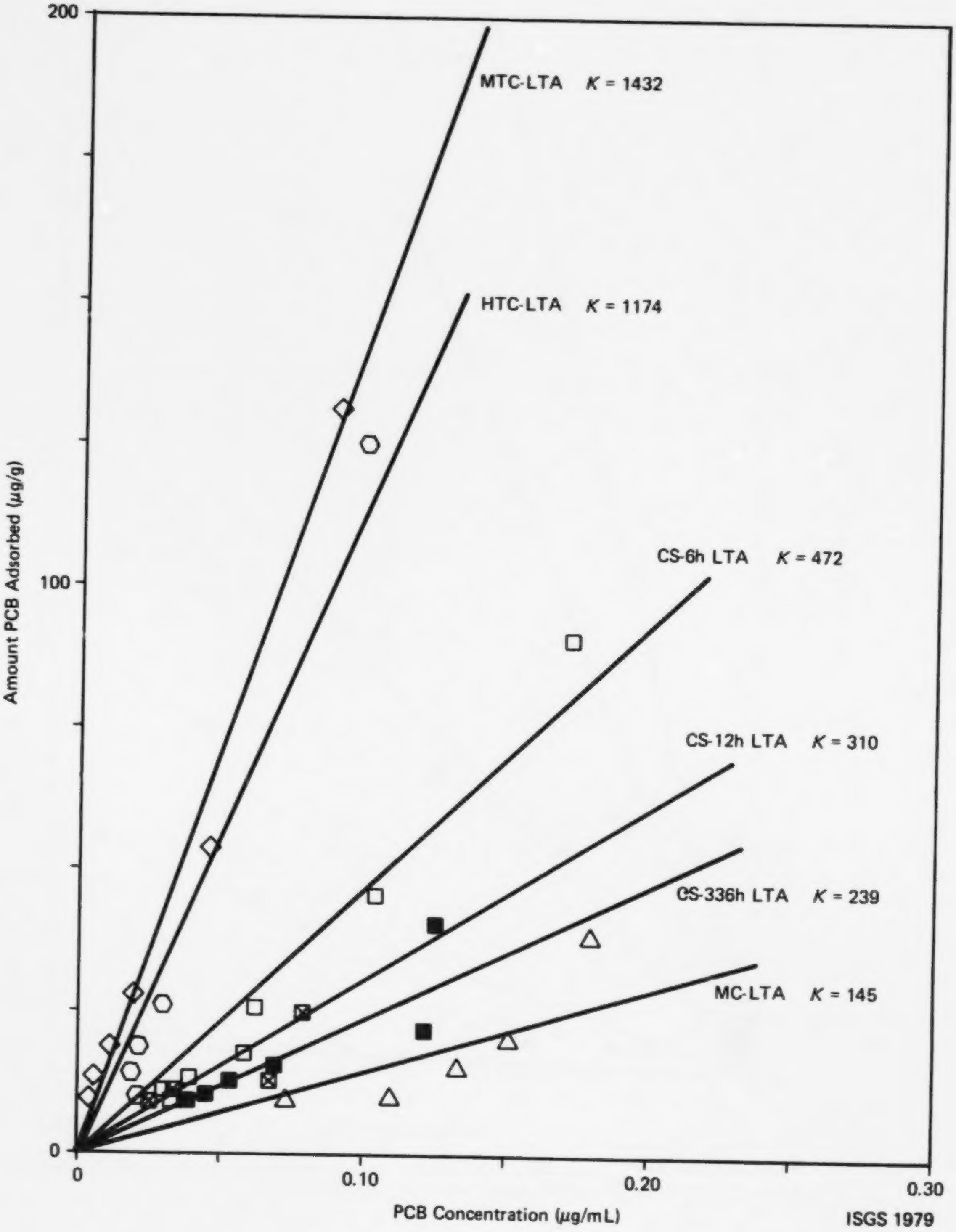

Figure 17. PCB adsorption by low-temperature ashes of earth materials

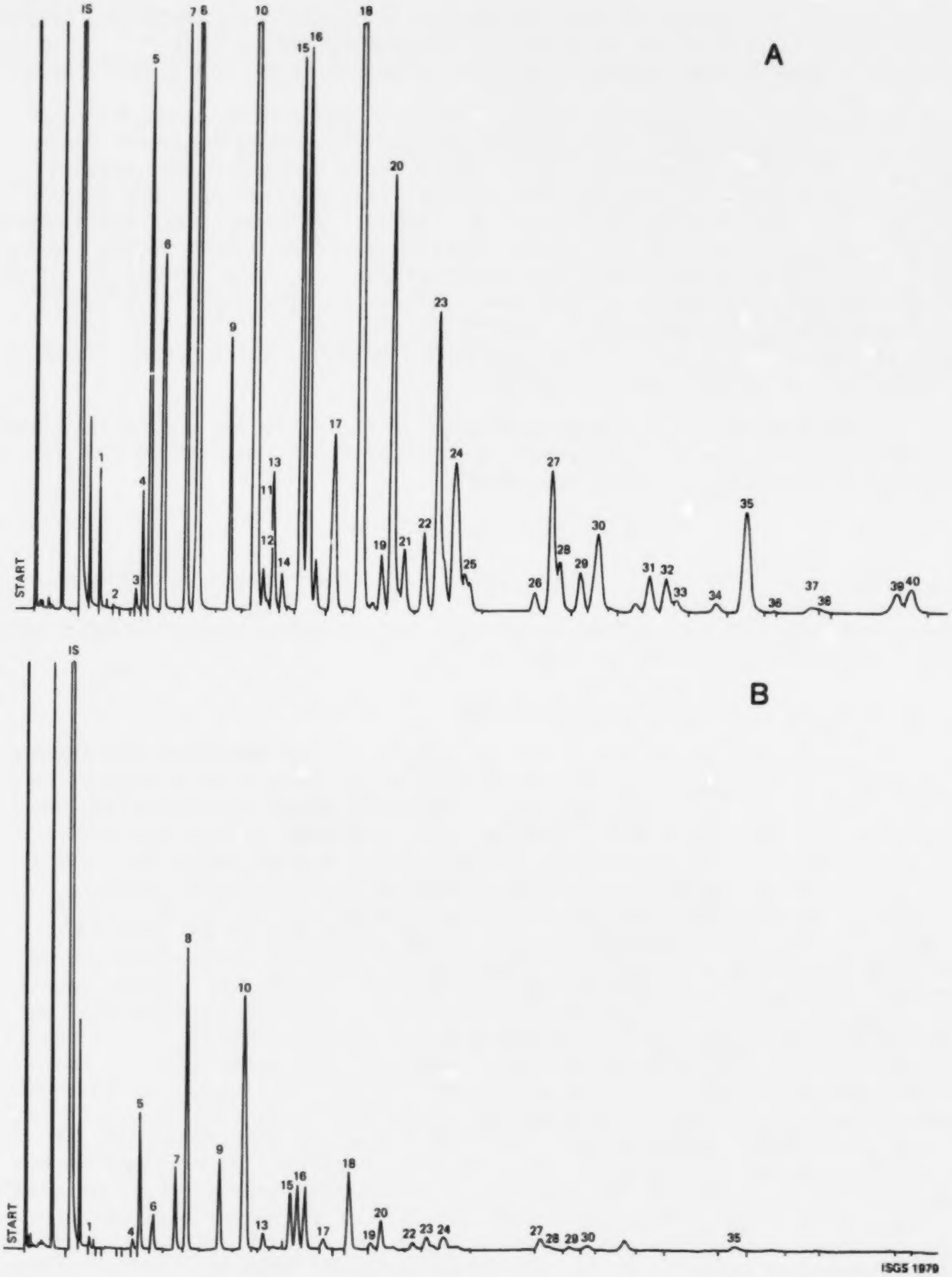

Figure 18. Capillary column analysis of Aroclor 1242 remaining in solution: (A) after adsorption on reaction bottle (blank); and (B) after adsorption by medium-temperature char

tion constant (K) unique to each adsorbent. Scharpenseel, Theng, and Stephen (1978) also found a linear relation for the adsorption of 2, 3, 4-trichlorobiphenyl from n-hexane solution by montmorillonite and humic acid.

A second result shown in Figure 16 is that there were no significant differences between adsorption of Aroclor 1242 and a used capacitor fluid by any of the five adsorbents. This result is in agreement with results reported previously for the solubilities of fresh Aroclor 1242 and used Aroclor 1242 capacitor fluid (Lee et al., 1978). No significant differences in the aqueous solubility or the distribution of isomers were found; therefore, no differences in adsorption would be expected. This result is significant because it shows that laboratory studies carried out with fresh Aroclor 1242 can be extrapolated to the field, where aged fluids that have gone through a "burn out" process are found, with a greater degree of confidence than previously was possible.

A third result illustrated in Figures 16 and 17 is the wide differences in adsorption of PCBs by the various earth materials. Adsorption for the five earth materials followed the series

$$MTC > HTC > CS > MC > OS.$$

Low-temperature ashing reduced the amounts of PCBs adsorbed by all samples. For the series of Catlin soil (CS) samples, the PCB adsorption decreased as the ashing time increased; this suggests a relationship between organic carbon content and adsorption of PCBs.

Capillary Column Analysis of Adsorption

A comparison of the adsorption of isomers in the water-soluble Aroclor 1242 solution by several different adsorbents was investigated by application of capillary column GC analysis. Figure 18 gives representative gas chromatograms of water-soluble Aroclor 1242 remaining in solution after adsorption by the reaction bottle (blank) and by medium-temperature char. The quantitative composition and percentage of individual PCB isomers remaining in solution after adsorption by several adsorbents is shown in Table 12. The total adsorption found by the summation of the individual isomers is plotted in Figure 16. The figure illustrates the close accord between the amounts of PCBs adsorbed in the two experiments. Other results in Table 12 indicate that 31 percent of the water-soluble Aroclor 1242 was adsorbed on the glass surface of the Wheaton reaction bottles. This result is in agreement with that of Gresshoff, Mahanty, and Gortner (1977) who also reported PCB adsorption on glassware. Zitko (1971) reported that water-soluble PCBs were strongly adsorbed by plastic surfaces such as polethylene sheets and tubes. Eichelberger (1971) also observed that 60 percent of Aroclors, ranging from 1232 to 1268, in water samples were adsorbed on the walls of the container or the silt contained in the river water. The results of this study also confirm the strong affinity of water-soluble PCBs for the surfaces of reaction and storage vessels. The glass surface preferentially adsorbed peaks 1, 4, 31, and 33 as shown in Table 12. This preferential adsorption of individual isomers also depends on the characteristics of the adsorbent. With high temperature char, peaks 3, 14, 31, and 34

TABLE 12. Quantitative distribution of PCB isomers after adsorption by several adsorbents as analyzed by capillary column GC analysis.

Peak no.	No. of Cl	Identification	AR1242 (ppb)	Blank		HTC (0.1987g)		MTC (0.2081g)	
				(ppb)	% remaining[a]	(ppb)	% remaining[b]	(ppb)	% remaining[b]
1	1	2-	121.59	47.67	39.21	21.47	45.04	5.82	12.21
2	1	3-							
3	1	4-	15.07	9.03	59.92	1.14	12.62	0.13	1.44
4	2		9.06	3.76	41.50	1.49	39.63	0.42	11.17
5	2	2,2′-	21.18	18.04	85.17	8.30	46.01	4.94	27.38
6	2	2,4-	23.76	20.62	86.78	5.25	25.46	2.15	10.43
7	2	2,3′-	30.60	24.85	81.21	7.25	29.18	3.56	14.33
8	2	2,4′-	138.93	105.58	76.00	31.63	29.96	13.78	13.05
9	3	2,6,2′-	8.33	6.70	80.43	3.16	47.16	2.39	35.67
10	3	2,5,2′-	61.35	49.58	80.81	15.67	31.61	8.86	17.87
11	3		2.15	1.38	64.19	0.21	15.22	0.05	3.62
12	3		0.48						
13	3	2,4,2′-	4.50	4.00	88.89	1.03	25.75	0.50	12.50
14	2	3,4′-	2.98	2.37	79.53	0.16	6.75	0.14	5.91
15	2&3	4,4′-& 2,3,2′-	35.30	27.32	77.39	5.78	21.16	3.38	12.37
16	3	2,4,3′-	27.47	17.94	65.31	3.47	19.34	2.16	12.04
17	3	2,4,4′-	9.87	8.47	85.82	1.05	12.40	0.55	6.49
18	3	2,5,4′-	65.07	50.19	77.13	6.82	13.59	3.19	6.36
19	3	3,4,2′-	2.59	2.28	88.03	0.55	24.12	0.28	12.28
20	4	2,5,2′,5′-	22.25	18.32	82.34	2.32	12.66	1.22	6.66
21	4		3.59	2.76	76.88	0.25	9.06	0.14	5.07
22	4		4.09	3.72	90.95	0.58	15.59	0.40	10.75
23	3&4	2,4,2′,5′-	19.51	14.41	73.86	1.47	10.20	0.64	4.44
24	4	2,4,2′,4′-	15.88	9.26	58.31	0.21	2.27	0.90	9.72
25	4		3.37	1.99	53.05	0.21	10.55	0.15	7.54
26	4		1.09	0.99	90.83	0.14	14.14	0.08	8.08
27	4	2,3,2′,5′-	12.83	7.21	56.20	0.89	12.34	0.67	9.29
28	4		3.13	2.28	72.84	0.25	10.96	0.21	9.21
29	4		2.50	2.06	82.40	0.27	13.11	0.15	7.28
30	4	2,5,3′,4′-	7.21	5.45	75.59	0.51	9.36	0.32	5.87
31	3		4.70	2.12	45.11	0	0	0	0
32	4		2.70	1.97	72.96	0.08	4.06	0.06	3.05
33	4		2.63	0.73	27.76	0	0	0	0
34	3		0.82	0.64	78.05				
35	4	2,4,3′,4′-	9.79	7.09	72.42	0.19	2.68	0.22	3.10
36	5								
37	5		0.99	0.59	59.60				
38	5								
39	5		2.47	1.76	72.26			0.06	3.41
40	5		2.84	1.92	67.61			0.04	2.08
Total			702.67	485.05	69.03	121.80	25.11	61.05	12.59

[a] % remaining compared with AR1242.

[b] % remaining compared with blank.

were the predominant mono-, di-, tri-, and tetra-chlorobiphenyl peaks being adsorbed. The percentages remaining, compared with the blank (glass surface), were 13, 7, 0, and 0, respectively. With medium temperature char, peaks 3, 14, 31, and 34 were the predominant mono-, di-, tri-, and tetra-chlorobiphenyl peaks being adsorbed. They represent 1, 6, 0, and 0 percent remaining, respectively. On the other hand, no preferential adsorption of particular isomers was apparent by either Catlin soil or sand, but both preferentially adsorbed higher chlorinated isomers as a class over lower chlorinated isomers.

TABLE 12. *Continued.*

Peak no.	No. of Cl	Identi- fication	HTC (0.0492g)		MTC (0.0511g)		CS (0.0546g)		Sand (0.0521g)	
			(ppb)	% remaining[b]	(ppb)	% remaining[b]	(ppb)	% remaining[b]	(ppb)	% remaining
1	1	2-	15.83	33.21	45.17	94.76	45.88	46.25	85.31	100
2	1	3-								
3	1	4-	4.36	48.28	1.87	20.71	6.88	76.19	12.06	100
4	2		1.13	30.05	2.94	78.19	3.38	89.89	6.09	100
5	2	2,2'-	9.45	52.38	10.77	59.70	13.90	77.05	18.85	100
6	2	2,4'	11.36	55.09	6.95	33.71	14.72	71.39	19.70	95.54
7	2	2,3'-	15.55	62.58	8.45	34.00	17.03	68.53	21.96	88.37
8	2	2,4'-	66.77	63.24	34.99	33.14	73.24	69.37	34.44	89.45
9	3	2,6,2'-	4.43	66.12	3.16	47.16	4.71	70.30	6.14	91.64
10	3	2,5,2'-	32.09	64.72	15.34	30.94	31.85	64.24	41.79	84.29
11	3		0.41	29.71	0.38	27.54	0.91	65.94	1.59	100
12	3									
13	3	2,4,2'-	2.37	59.25	1.01	25.25	2.46	61.50	3.40	85.0
14	2	3,4'-	0.92	38.82	0.24	10.13	1.36	57.38	2.17	91.56
15	2&3	4,4'-& 2,3,2'-	15.13	55.38	5.94	21.74	16.70	61.13	23.17	84.81
16	3	2,4,3'-	5.24	29.21	6.40	35.67	9.63	53.68	17.66	58.44
17	3	2,4,4'-	4.34	51.24	1.36	16.06	4.84	57.14	7.15	84.42
18	3	2,5,4'-	25.99	51.78	7.88	15.70	28.86	57.50	41.69	83.06
19	3	3,4,2'-	1.34	58.77	0.48	21.05	1.27	55.70	1.86	81.58
20	4	2,5,2',5'-	8.61	47.00	3.11	16.98	10.11	55.19	15.40	84.06
21	4		0.95	34.42	0.44	15.94	1.42	51.45	2.49	90.22
22	4		1.57	42.20	0.75	20.16	1.84	49.46	3.07	82.53
23	3&4	2,4,2',5'-	5.63	39.07	2.23	15.48	7.67	53.23	12.67	87.93
24	4	2,4,2',4'-	4.98	53.74	1.59	17.17	5.14	55.51	7.70	83.15
25	4		1.12	56.28	0.20	10.05	1.24	62.31	1.68	84.42
26	4		0.37	37.37	0.11	11.11	0.46	46.46	0.76	76.77
27	4	2,3,2',5'-	2.96	41.05	1.21	16.78	3.08	42.72	5.88	81.55
28	4		0.44	41.23	0.34	14.91	0.96	42.11	1.86	81.58
29	4		0.94	45.63	0.29	14.08	1.01	49.03	1.66	80.58
30	4	2,5,3',4'-	2.16	39.63	0.71	13.03	2.63	48.26	4.48	82.20
31	3		0.28	13.21	0.07	3.30	0.83	39.15	2.53	100
32	4		0.81	41.12	0.13	6.60	1.11	56.35	1.63	82.74
33	4				0.22	30.14			1.45	100
34	3		0.27	42.19	0.05	7.81	0.31	48.44	0.55	85.94
35	4	2,4,3',4'-	2.53	35.68	0.61	8.60	3.29	46.40	5.93	83.64
36	5									
37	5		0.13	22.03			0.39	66.10	0.57	96.61
38	5									
39	5		0.61	34.66			0.69	39.20	1.45	82.39
40	5		0.58	30.21	0.05	2.60	0.74	38.54	1.66	86.46
Total			254.8	52.53	165.44	34.11	320.54	66.08	478.45	98.64

[a] % remaining compared with AR1242.

[b] % remaining compared with blank.

In general, the higher chlorinated isomers were more adsorbable than the lower chlorinated isomers. Haque and Schmedding (1976) indicated the extent of adsorption for the surfaces they studied followed the sequence hexachloro- > tetrachloro- > dichloro-biphenyl for the isomers chosen. This preferential adsorption also depends on the position of the chlorine atom on the biphenyl ring; some particular isomers appeared to be more adsorbable than others in this study. They were peaks 1, 3, 4, 14, 31, and 33(Table 12).

Peaks 1, 3, and 14 were specifically identified as 2- and 4- monochlorobiphenyl, and peak 14 as 3, 4'-dichlorobiphenyl. Peaks 4, 31, and 33 were identified only as a di-, tri-, and tetra-chlorobiphenyl, respectively.

The adsorption of each class of isomers is illustrated by the adsorption data for medium-temperature char in Figure 19. In this figure, the average adsorption for all isomers such as monochloro-, and dichloro- have been considered together. It is clear that the higher chlorinated isomers were preferentially adsorbed.

Earth Material Properties Affecting Adsorption

The relation between total organic carbon (TOC) content and PCB adsorption was investigated. The PCB adsorption constant (K) plotted as a function of TOC is shown in Figure 20. A very highly significant (.001 level) correlation was found with a linear regression relation of

$$K = 255 + 18.5 \text{ TOC}$$

$$r^2 = 0.87.$$

Thus, the PCB adsorption constant (K) can be estimated from a knowledge of the TOC content of the earth material.

The relation between surface area (SA) of the adsorbents and PCB adsorption was also investigated. Surface area was measured using three adsorbates, nitrogen, carbon dioxide, and ethylene glycol. As is evident from the data in Table 1, each method can yield large differences in surface area depending on the surface characteristics of the particular adsorbent. Nitrogen adsorption gives a measure of the external surface area and does not penetrate pores smaller than about 5 angstroms in diameter. Carbon dioxide also measured external surface area, but is able to penetrate pores smaller than about 5 angstroms in diameter. The difference between these two measurements is particularly evident for the medium-temperature char sample, which has a nitrogen area of 1.6 m^2/g and a carbon dioxide area of 253 m^2/g. This large difference is interpreted as a measure of the large proportion of micropores (< 5 Å) contained in the medium-temperature char. This can be contrasted to the soil materials, which exhibited relatively small differences in surface area between the nitrogen and carbon dioxide measurements.

The third method of measurement was ethylene glycol adsorption. Ethylene glycol penetrates the interlayer region of swelling clays such as montmorillonite and gives a measure of the total surface area in these types of samples. The difference between the external area measured by nitrogen and the area measured by ethylene glycol gives an estimate of the "internal" or "interlayer" surface area. It is evident that the interlayer surface area is very high for the montmorillonite clay (Table 1).

The PCB adsorption constant (K) plotted as a function of CO_2-surface (SA) is shown in Figure 21. A highly significant (.001 level) correlation was found with a linear regression relation of

$$K = 230 + 6.64 \text{ SA}$$

$$r^2 = 0.82.$$

Very poor correlations were obtained using nitrogen and ethylene glycol surface areas. This is interpreted to indicate that PCB molecules were not able to penetrate into the interlayer surface regions of montmorillonite clay to be adsorbed. Thus, the PCB adsorption constant (K) could be estimated from CO_2-SA values. This result may be fortuitous since the CO_2-SA values parallel the TOC values. More studies are needed to confirm this result.

A three-variable regression analysis of the PCB adsorption constant (K), TOC, and CO_2-SA were investigated and the results are shown in Figure 22. A highly significant (.001 level) correlation was obtained with a linear regression relation of

$$K = 188 + 3.36 \text{ SA} + 11.4 \text{ TOC}$$

$$r^2 = 0.95.$$

The magnitude of the coefficients for SA and TOC indicate that TOC is the dominant property by a factor greater than three. The best estimates of K were obtained by a knowledge of both SA and TOC; however, if only one soil property must be chosen to estimate K, the TOC should be the property of choice. Care should be taken when applying this equation since K may be over-estimated for soils with low TOC content.

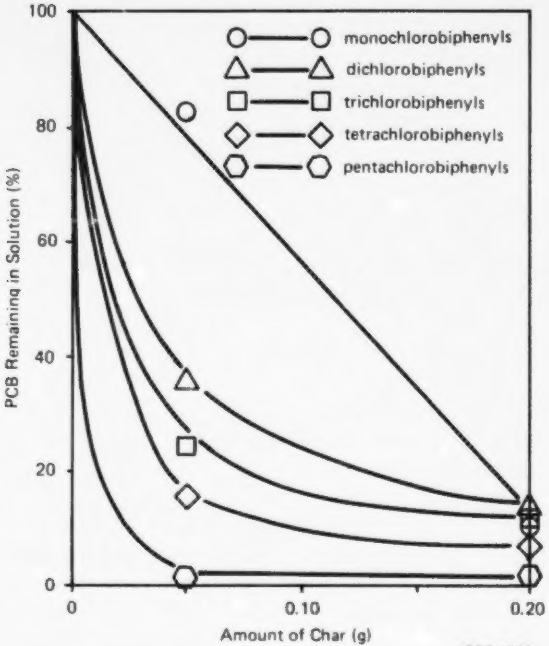

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Figure 19. The percentage of isomers in water-soluble Aroclor 1242 remaining in solution after adsorption by medium-temperature char

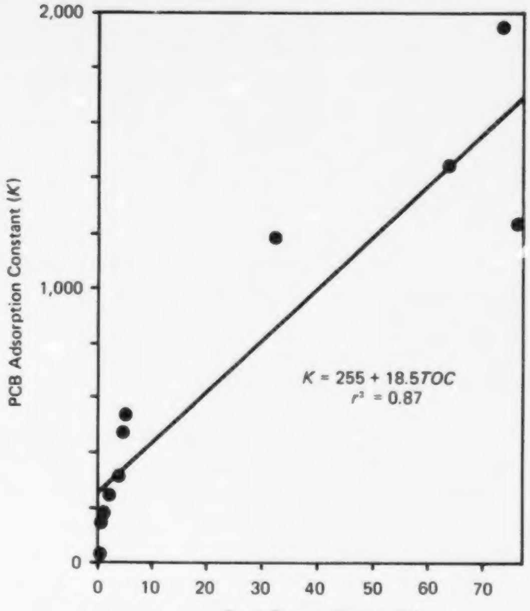

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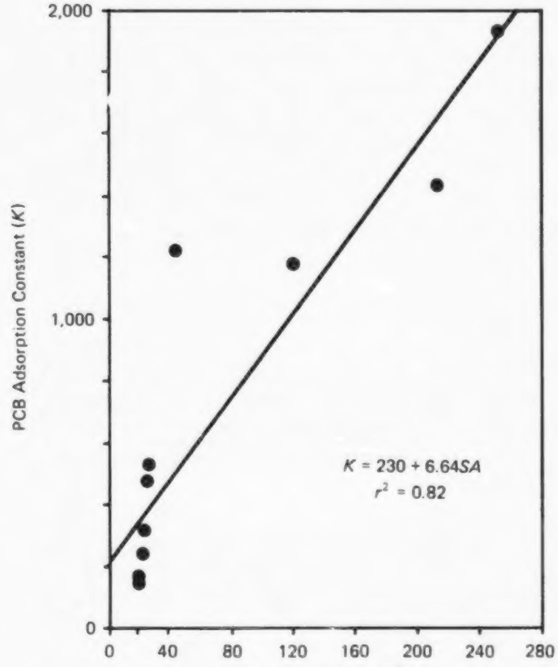
Figure 20. PCB adsorption constant (K) as a function of total organic carbon content (TOC)



ISGS 1979

Figure 21. PCB adsorption constant (K) as a function of surface area (SA)

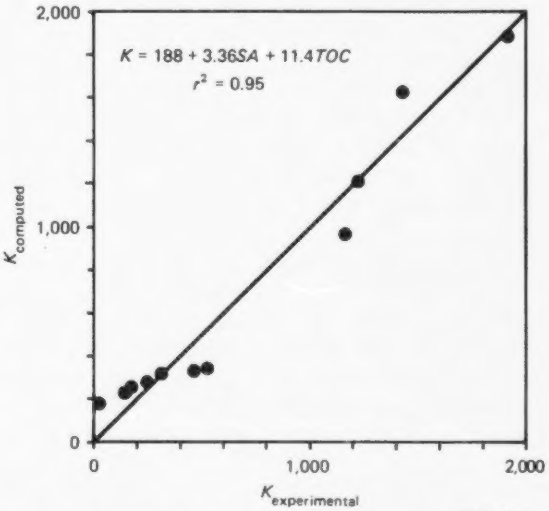


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Figure 22. Three-variable regression analysis of the PCB adsorption constant (K) as a function of total organic carbon content (TOC) and surface area (SA); $K_{computed}$ as a function of $K_{experimental}$

SECTION 7

MOBILITY OF PCBs AND DICAMBA IN SOIL MATERIALS: DETERMINATION BY SOIL THIN-LAYER CHROMATOGRAPHY[1]

RESULTS AND DISCUSSION

R_f values obtained from autoradiography were compared with those obtained by zonal extraction. The agreements were excellent. Autoradiography was especially satisfactory for soil TLC studies, as it provides a qualitative picture of movement (for example, diffusion, tailing) while allowing measurement of frontal R_f. Zonal extraction gave a more quantitative picture of PCB movement. Also detected by the zonal extraction procedure are tailing, the origin spot, and the frontal movement of the compound; however, definition of the concentration profile is limited by the length of the soil segment chosen and by the extraction and analytical efficiencies. In summary, the two methods gave essentially identical pictures of PCB movement on TLC plates.

The mobilities of Aroclor 1242, Aroclor 1254, and Dicamba in several earth materials expressed as frontal R_f values are summarized in Table 13. The data for capacitor fluid were identical to Aroclor 1242 and are not shown in Table 13. The data show that under the conditions tested, Aroclor 1242 and Aroclor 1254 (and the capacitor fluid) stayed immobile in these soil materials when leached with water or Du Page leachate, but were highly mobile when leached with carbon tetrachloride. Dicamba showed the reverse trend, being highly mobile in water and in Du Page leachate and quite stationary when leached with carbon tetrachloride.

A closer look at the structure of Dicamba and PCB will help explain the mobilities observed. Dicamba is 3,6-dichloro-o-anisic acid. Because Dicamba has two polar groups (-COOH and $-OCH_3$), hydrogen bonding can occur between the water molecules and the carboxyl and methoxy groups of Dicamba; this increases the solubility of Dicamba in polar solvents like water and leachate. Solubility of Dicamba in water is 4,500 ppm (Herbicide Handbook, 1974).

PCBs are nonpolar in nature and are only very slightly soluble in polar solvents like water. Solubility of Aroclor 1242 in water has been determined to be 200 ppb (Tucker, Litschgi, and Mees, 1975), and Aroclor 1254,

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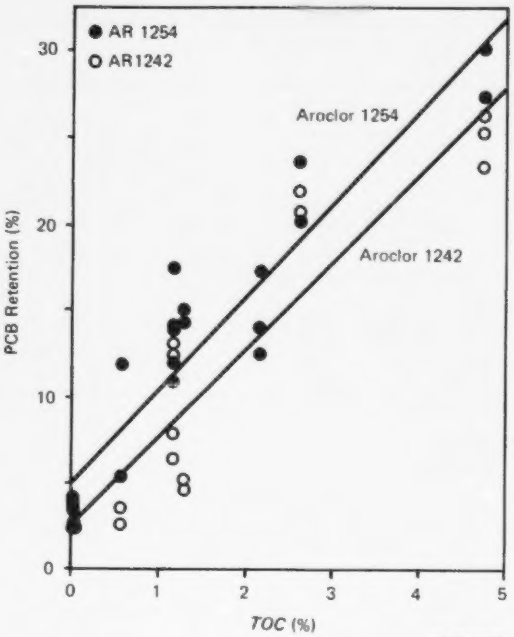
TABLE 13. Mobility of Aroclor 1242, Aroclor 1254, and Dicamba in several soil materials leached with various solvents as measured by soil TLC.

	R_f values								
	H_2O			DuPage leachate			CCl_4		
	Aroclor 1242	Aroclor 1254	Dicamba	Aroclor 1242	Aroclor 1254	Dicamba	Aroclor 1242	Aroclor 1254	Dicamba
Ava Silty clay loam	.02	.02	1.00	.02	.02	1.00	1.00	.96	.02
Bloomfield Loamy sand	.03	.03	1.00	-	-	-	-	-	-
Catlin Silt loam	.02	.02	.85	.04	.04	.90	1.00	1.00	.02
Catlin Loam	.02	.02	1.00	.03	.03	1.00	1.00	1.00	.03
Cisne Silt loam	.03	.02	1.00	.03	.02	.99	1.00	1.00	.05
Coal char (1200°F)	.03	.03	.79	.04	.04	.80	1.00	1.00	.03
Drummer Silt loam	.03	.03	0.99	-	-	-	1.00	1.00	.03
Flanagan Silt loam	.02	.02	1.00	.06	.05	1.00	1.00	1.00	.02
Ottawa Silica sand	.03	.03	1.00	.03	.03	1.00	1.00	1.00	.02

56 ppb (Haque, Schmedding, and Freed, 1974); however, PCBs are quite soluble in organic solvents like acetone, methanol, benzene, or carbon tetrachloride. Mobilities of Aroclor 1242, Aroclor 1254 and Dicamba were tested in silica gel leached with acetone, methanol, benzene, carbon tetrachloride, and mixtures of water-acetone and water-methanol. The results are given in Table 14. Consistent with the soil TLC data obtained by leaching with carbon tetrachloride, R_f values of 1.00 were obtained using the organic solvents. The data also indicated that relatively small amounts of water (9 percent) in the methanol-water mixture significantly reduced the mobility of the PCBs compared to pure methanol. Dicamba mobility followed the inverse trend. It was quite clear that mobilities of PCBs and Dicamba in soil materials and silica-gel were highly related to the solubility of PCBs and Dicamba in the solvent with which the TLC plates were being leached.

The above finding has great significance in the disposal of PCB wastes. To prevent potential migration of PCBs in a landfill, PCB wastes and organic solvents should not be disposed of in the same landfill location, and the PCBs should not be allowed to come in contact with leaching organic solvents.

The mobility of PCBs in carbon tetrachloride can be correlated with characteristics of the earth materials such as clay content, surface area, PH, cation exchange capacity, and organic matter. The zonal extraction technique yields a quantitative measure of the quantity of PCB that moves to the top of each soil TLC plate with the solvent. Although PCBs have R_f values of 1.00 for all the soil materials leached with carbon tetrachloride (Table 13), the percentage of PCBs that were retained against leaching on the lower part of the TLC plates differs for each of the soil materials. The mobility measured in this manner was correlated with soil material properties (Table 15).



ISGS 1979

Figure 23. Retention of PCB in soils leached with carbon tetrachloride as a function of total organic carbon (TOC) content of the soils

The relation between the total organic carbon content of the soils and retention of PCB by soils leached with carbon tetrachloride was investigated, and the results are plotted in Figure 23. The plots indicate there is a tendency toward higher percentages of retention of Aroclor 1254 compared to Aroclor 1242. This hypothesis was tested using the paired t-test statistic (Texas Instruments, 1975) for pairs of data from the same soil. The result was a highly significant (.01 level) difference between the mobility of Aroclors 1242 and 1254 in carbon tetrachloride solution, Aroclor 1254 being less mobile. This result is in agreement with Tucker, Litschgi, and Mees (1975), Haque and Schmedding (1976), and Lee et al. (1979) who found the higher-chlorinated PCB isomers had a higher affinity for soil materials than the lower-chlorinated isomers.

The results of linear regression analysis of the data shown in Figure 23 is tabulated in Table 15. The data yielded a highly significant (.001 level) correlation between retention of PCBs by soil and the TOC content. The coefficients of determination (r^2) were 0.87 and 0.84 for Aroclors 1242 and 1254, respectively. These results are also congruent with those of several other workers who have noted a relation between PCB retention and the organic matter in soils (Briggs, 1973; Iwata, Westlake, and Gunther, 1973; Tucker, Litschgi, and Mees, 1975; Scharpenseel, Theng, and Stephan, 1978; Lee et al., 1979).

Also included in Table 15 are the results of linear regression analysis of the effect of surface area on mobility of PCBs. The results indicate no significant correlation with nitrogen surface area values, but significant correlations were obtained using carbon dioxide and ethylene glycol surface

TABLE 14. Mobility of Aroclor 1242, Aroclor 1254, and Dicamba on silica-gel TLC plates using various leaching solvents.

	R_f values		
Leaching solvent	Aroclor 1242	Aroclor 1254	Dicamba
Deionized H_2O	0.15	0.15	0.95
Du Page leachate	0.15	0.15	0.80
80% H_2O–20% acetone	0.09	0.06	0.30
Acetone	1.00	1.00	0.88
15% H_2O–85% methanol	0.79	0.79	0.71
9% H_2O–91% methanol	0.80	0.83	0.70
Methanol	1.00	1.00	-
Benzene	0.99	0.95	0.09
Carbon tetrachloride	1.00	1.00	0.03

TABLE 15. Results of linear regression analysis of retention of Aroclor 1242 and Aroclor 1254 by soils against leaching with carbon tetrachloride (R) versus the soil properties of total organic carbon (TOC) content and surface area measured by adsorption of nitrogen (N_2-SA), carbon dioxide (CO_2-SA), and ethylene glycol (EG-SA) expressed as values of the coefficient of determination (r^2).

	r^2 values	
	Aroclor 1242	Aroclor 1254
R vs. TOC	0.87^a	0.84^a
R vs. N_2-SA	0.03^{NS}	0.09^{NS}
R vs. CO_2-SA	0.54^b	0.54^b
R vs. EG-SA	0.74^a	0.43^c
R vs. TOC, CO_2-SA	0.90^a	0.89^a
R vs. TOC, EG-SA	0.93^a	0.87^a

[NS] Not significant
[a] Significant at 0.001 level
[b] Significant at 0.05 level
[c] Significant at 0.1 level

area values. Highly significant correlations were obtained by including both surface area and TOC content in regressions with the mobility of the two Aroclors (Table 15).

The lack of strong correlations and the variability in the results using the surface area data precludes a conclusion as to the ability of PCB molecules in carbon tetrachloride solution to penetrate into the interlayer region of expandable clays or as to the significance of the surface area of soils in retarding PCB migration. There is, however, a clear relation between the TOC content of the soils and their ability to retard PCB migration.

SECTION 8

DEGRADATION OF PCBs BY MIXED MICROBIAL CULTURES[1]

RESULTS AND DISCUSSION

Preliminary Work

The first mixed culture to be grown, the C-line, yielded the yellow-colored intermediate described by Furukawa and Matsumara (1976) in about 5 weeks; the S-line took about 2 weeks and the N-line, less than 1 week to turn the solutions yellow. Because the S-line had some previous exposure

TABLE 16. Results after 15 and 45 days of degradation using culture grown in acetic acid.

		Percentage of removal of peak when compared to blanks		
Peak number	Number of Cl	15 days (%)	45 days (%)	Retention time in Fig. 25 (min)
2	1	100	100	10.43
4	2	29	28	15.30
5	2	14	23	15.97
6,7	2	100	100	16.96
8	2	100	100	17.19
9	2	62	62	18.96
11	2	37	37	19.74
13	3	0	0	22.04
15	3	0	0	23.55
16	3	0	0	24.56
17	2 and 3 mixture	0	0	25.83
18	3	22	23	26.12
22	3	29	56	27.40
24	3	10	13	28.29
25	4	0	0	29.45
26	4	-	-	29.90
27	4	0	0	30.65
28	3	100	85	30.96
32	4	0	0	31.77
34	4	0	0	34.34
37	4	31	34	35.37
41	4	0	0	38.35
44,45	4	0	0	40.96
Total degradation		43	44	

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[1] Authors: R. R. Clark, E.S.K. Chian, and R. A. Griffin

to PCBs before isolation and the N-line had much more exposure, it appears that the presence of PCBs in a particular environment enhances the selection of microorganisms capable of degrading PCBs. In view of this, the mixed cultures were grown on biphenyl for more than 7 months to ensure that the cultures were highly selective toward biphenyl-degrading organisms before the PCB degradation experiments were conducted.

The first PCB degradation studies were run for 15, 30, and 45 days. Figure 24 shows a chromatogram of the 15-day extract. Figure 25 shows the chromatogram of the 15-day blank. Table 16 lists the peaks found in the PCB samples. Occasionally peaks cannot be resolved, therefore these are combined in the tables. As can be seen, all of the monochloro and most of the dichlorobiphenyls are easily degraded. It also appears that most of the degradation occurred prior to 15 days.

The results, however, were suspect because the mixed culture was grown in acetic acid for 3 days prior to being added to the PCB solution under study to eliminate the biphenyl in the solution. This procedure could have made the mixed culture less able to degrade the PCBs because the selective pressure toward a biphenyl-degrading culture was eased.

Table 17 lists the results of a 7-day study of PCB degradation using both a mixed culture grown only on biphenyl and one grown on acetic acid for

TABLE 17. Comparison of mixed cultures grown on biphenyl only and those grown on acetic acid.

		Percentage of removal after 7 days when compared to blanks	
Peak number	Number of Cl	Biphenyl only (%)	Acetic acid grown (%)
2	1	100	100
3	1	100	100
4	2	100	7
5	2	81	13
6,7	2	100	100
8	2	100	100
11	2	100	20
13	3	0	0
15	3	19	0
16	3	0	0
17	2 + 3	66	0
18	3	100	0
22	3	100	15
24	3	93	0
25	4	33	0
27	4	0	0
28	3	100	68
32	4	0	0
33	4	0	0
34	4	0	0
Total degradation		82	30

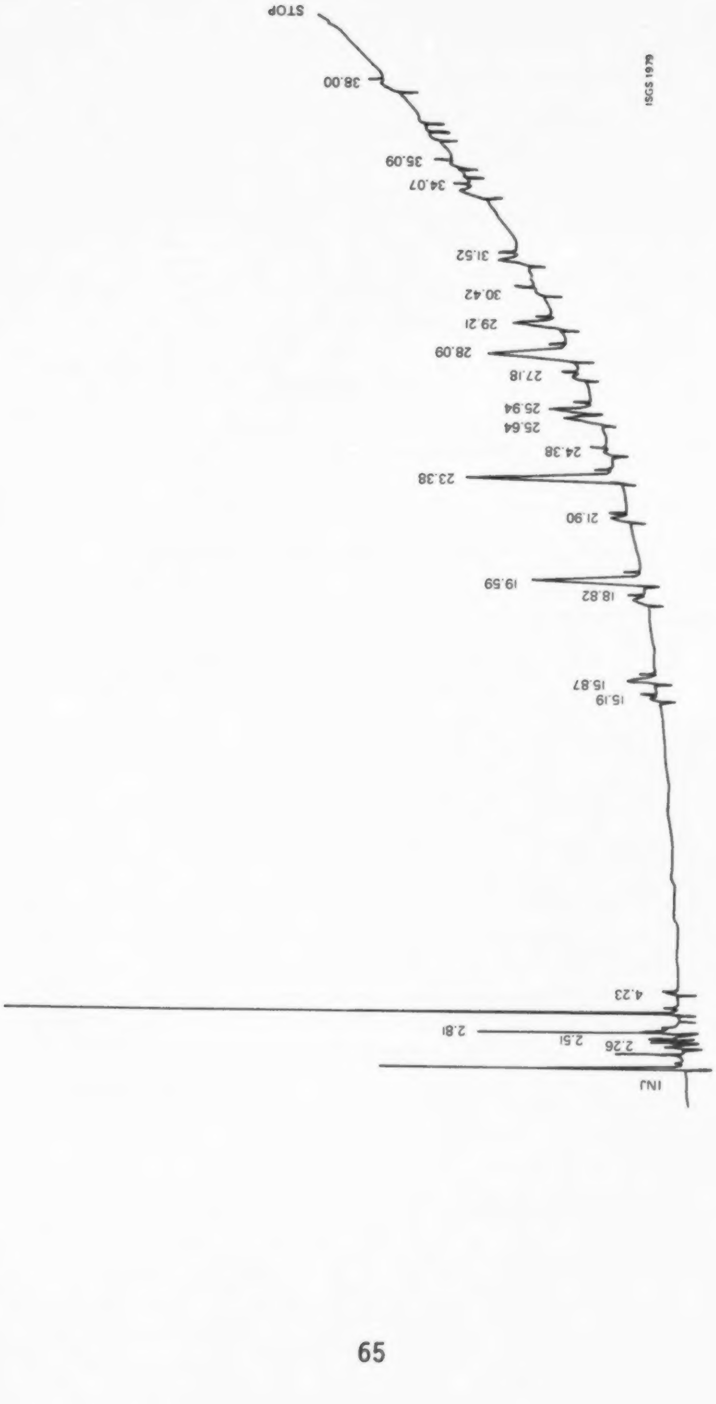

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Figure 24. Water-soluble Aroclor 1242 after 15 days of degradation

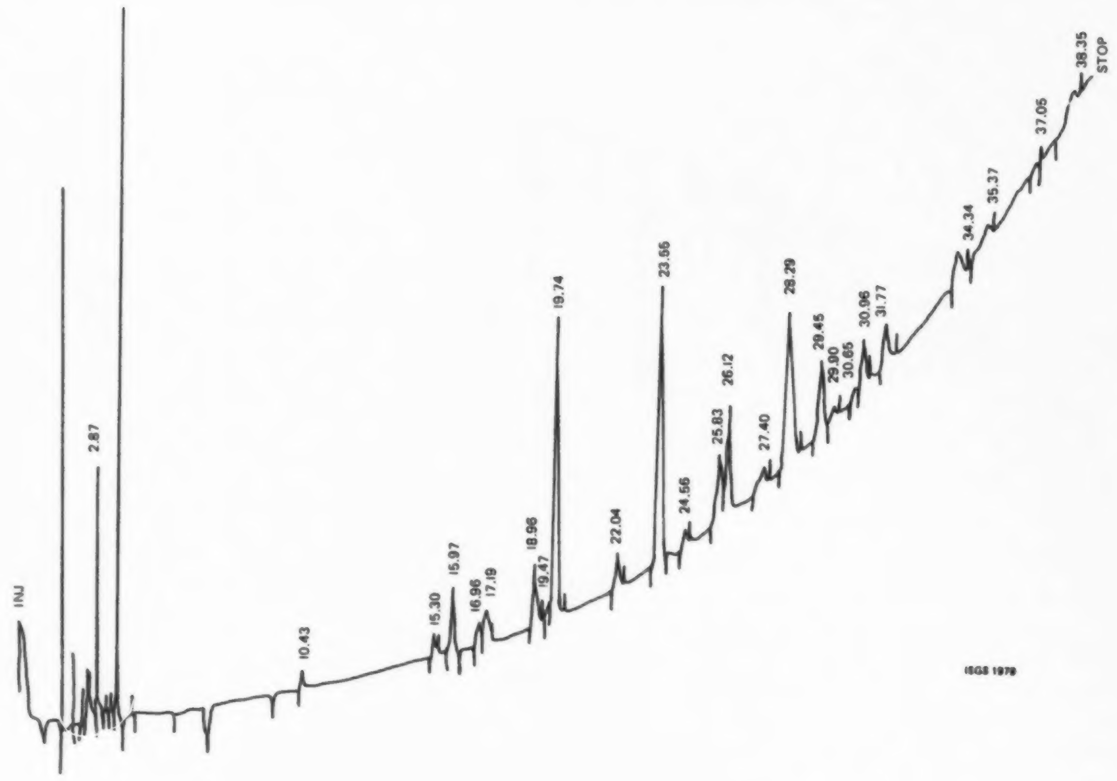

Figure 25. Original water-soluble Aroclor 1242 solution prior to degradation

3 days prior to the experiment. The culture grown only on biphenyl did much better than the culture grown on acetic acid for 3 days. These results indicate that the data in Table 16 may not be quantitatively correct, but are probably qualitatively correct in that most of the degradation occurred in less than 15 days.

The data in Table 17 show that all the mono- and dichloro-biphenyl isomers (except peak number 15) were easily degraded in 7 days. Also, many of the trichlorobiphenyl isomers were degraded, but some were resistant to degradation. Almost all of the tetrachlorobiphenyl isomers were not degraded in 7 days.

Sonification Study

To determine if the extraction procedure would extract all the PCBs in solution, a 2-day degradation sample of the S-line culture was run and sonified before extraction. In this way, the PCBs that are inside the microorganisms would be extracted. If the pH 2 extraction did not extract all of the PCBs inside the microorganisms, then the sonified extract would show higher amounts of PCB isomers and/or more isomer peaks because of isomers that could not be extracted with the pH 2 extraction. Table 18 shows the results of the sonification study. The sonified extract showed a greater amount of PCB removal than did the pH 2 extract. This difference may not be significant since the error in the analysis may be more than the difference between the two samples. Volatilization of PCBs due to localized heating of the solution near the sonifier tip is another possible explanation. In addition, all peaks that were missing in the pH 2 extract were missing in the sonified extract. Because of this, it was felt that the pH 2 extraction procedure adequately represented the degradation of PCBs that was occurring in the solutions.

Comparison of the Three Mixed Cultures

Degradation samples were run for 5, 10, and 15 days using Aroclor 1242 saturated solution inoculated with 3-day old N-, C-, or S-line cultures. Figure 26 shows a comparison of a 5-day blank and 5-day degradation using the S culture. Figure 27 shows a 5-day blank, and Figure 28, a 5-day degradation, both using the N culture. Note that the analyses were performed using a different capillary column. The C culture was also analyzed on the same capillary column as the N culture, therefore the chromatograms resembled the N-culture chromatograms. As can be seen from these figures, the S-culture degradation may not be directly comparable to the C- and N-culture degradation because of differences in the capillary column. Table 19 compares the amount of degradation for each culture at 5 and 15 days. Some peaks were not reproducibly present, so no percentage of degradation is reported for them. Because of analytical difficulties, for those isomers yielding very small peaks, degradation of less than 20 percent was not considered significant. For most of the peaks the degradation was the same for 5 as for 15 days; this observation indicated that most of the degradation occurred in less than 5 days.

TABLE 18. Comparison of sonified extracts and pH 2 extracts.

		Percentage of degradation	
Peak number	Number of Cl	pH 2 extract	Sonified extract
2	1	100	100
3	1	100	100
4	2	54	75
5	2	45	68
6,7	2	100	100
8	2	95	99
9	2	100	100
10	3	0	34
11	3	8	39
12	3	29	45
13	3	28	51
14	2	100	100
15	2 + 3	27	48
16	3	56	70
17	3	13	0
18	3	74	82
19	3	66	75
20	3	100	100
21	3	0	17
22	4	16	35
23	4	-	-
24	4	100	100
25	4	0	19
26	3	100	100
27	4	0	0
28,29,30	4	0	7
31	4	17	80
32	4	0	10
33	4	0	10
34	4	0	11
35	4	0	13
36,37	4	0	21
38	4	2	4
39	4	38	49
40	3	5	65
41	4	5	2
42	4	-	-
43	4	-	-
44	4	-	-
45	4	-	-

Most of the isomers were degraded to the same degree with all three mixed cultures; however, some were degraded to different extents. Differences in degradation can be due to different mechanisms or pathways of degradation (Ahmed and Focht, 1973a; Baxter et al., 1975; Furukawa, Tonomura, and Kamibayashi, 1978). The usual patterns reported in other literature—monochlorobiphenyls are easily degraded, dichlorobiphenyls are slightly less degradational, and tetrachlorobiphenyls are not readily degraded—are seen in the data reported here. In this study, however, the degradation occurred more rapidly than previously reported (Ahmed and Focht, 1973a; Baxter et al., 1975; Furukawa and Matsumura, 1976; Furukawa, Tonomura, and Kamibayashi, 1978; Sundstrom, Hutzinger, and Safe, 1976; Tucker, Saeger, and Hicks, 1975; Mihashi et al., 1975).

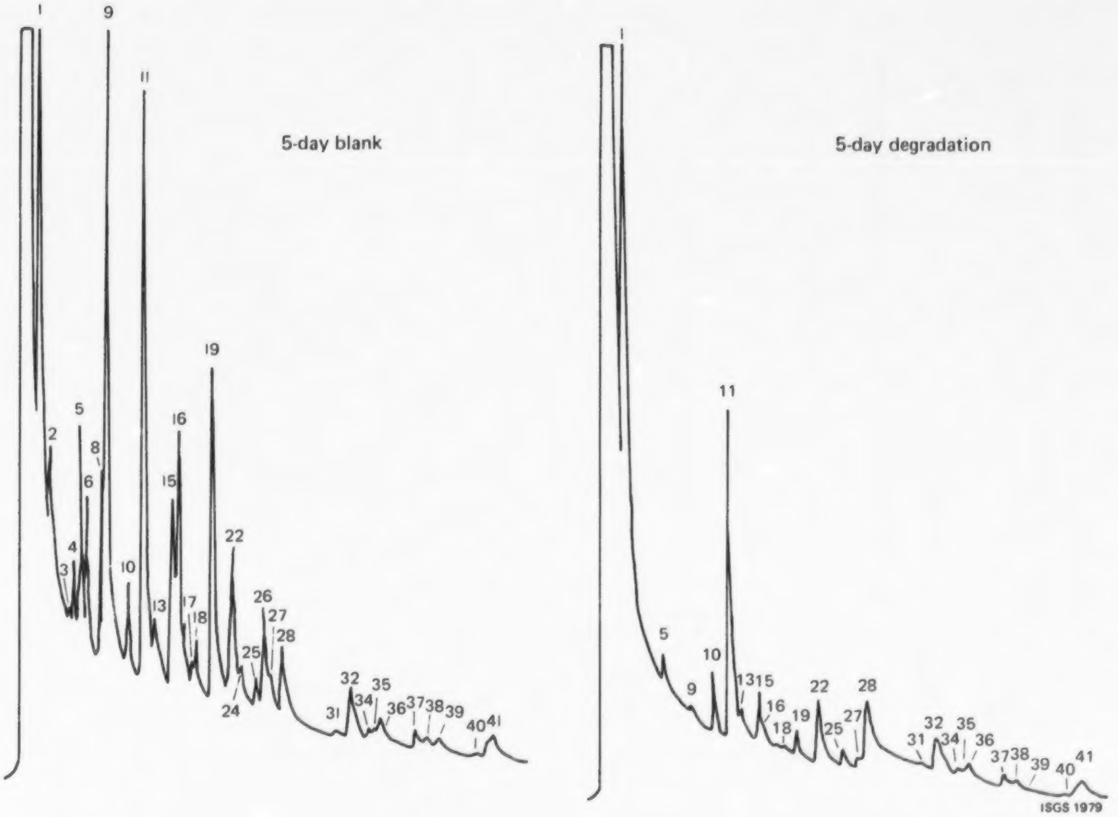

Figure 26. Comparison of 5-day blank and 5-day degradation of Aroclor 1242 using the S culture

Kinetic Study

A degradation study was run using the N culture for 3, 6, 12, 24, and 48 hours. Two samples and two blanks were taken at each time increment. Table 20 shows the results of this study. As with previous studies, the lower chlorinated isomers were degraded most rapidly. Many of the isomers showed increasing amounts of degradation with each time increment. Six of the peaks are plotted in Figures 29 and 30. The rates of degradation are somewhat different for different isomers; even isomers with the same number of chlorines per molecule have different rates of degradation. This difference has also been reported by Baxter et al., (1975). This finding would indicate that the position of substitution has a bearing on the degradational properties of a particular isomer. Even with the use of a capillary column, each particular peak may not be a pure isomer; a peak

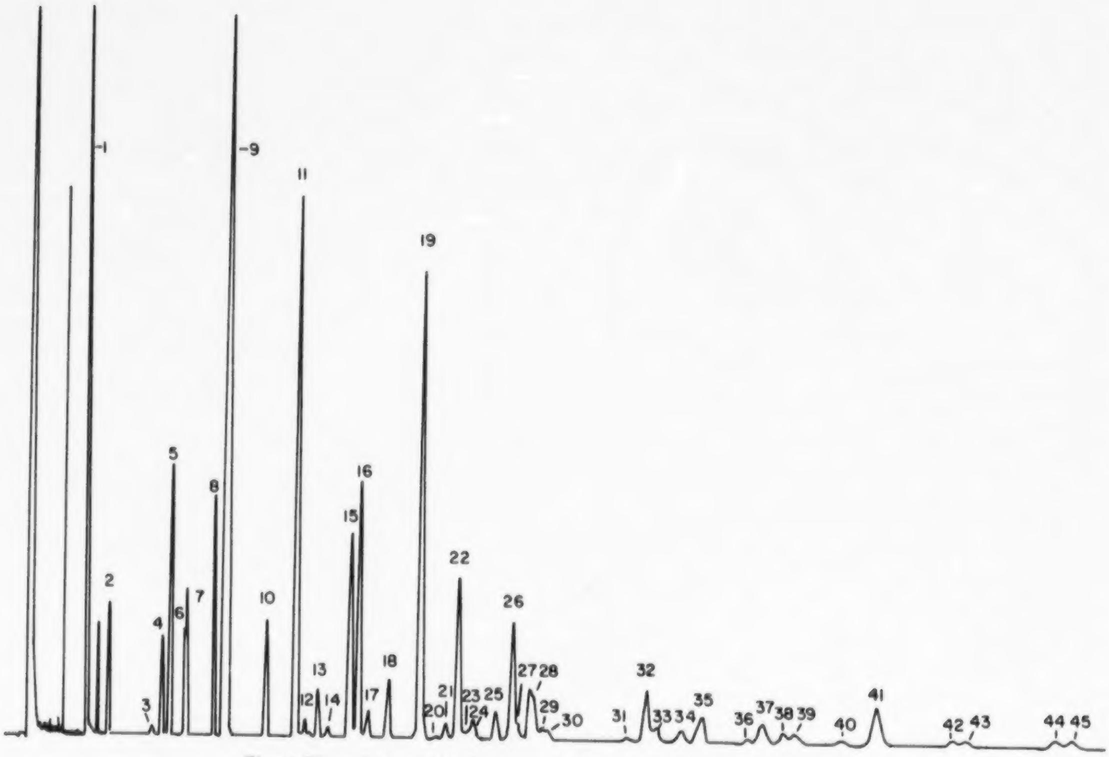

Figure 27. Results of 5-day blank of Aroclor 1242 using the N culture

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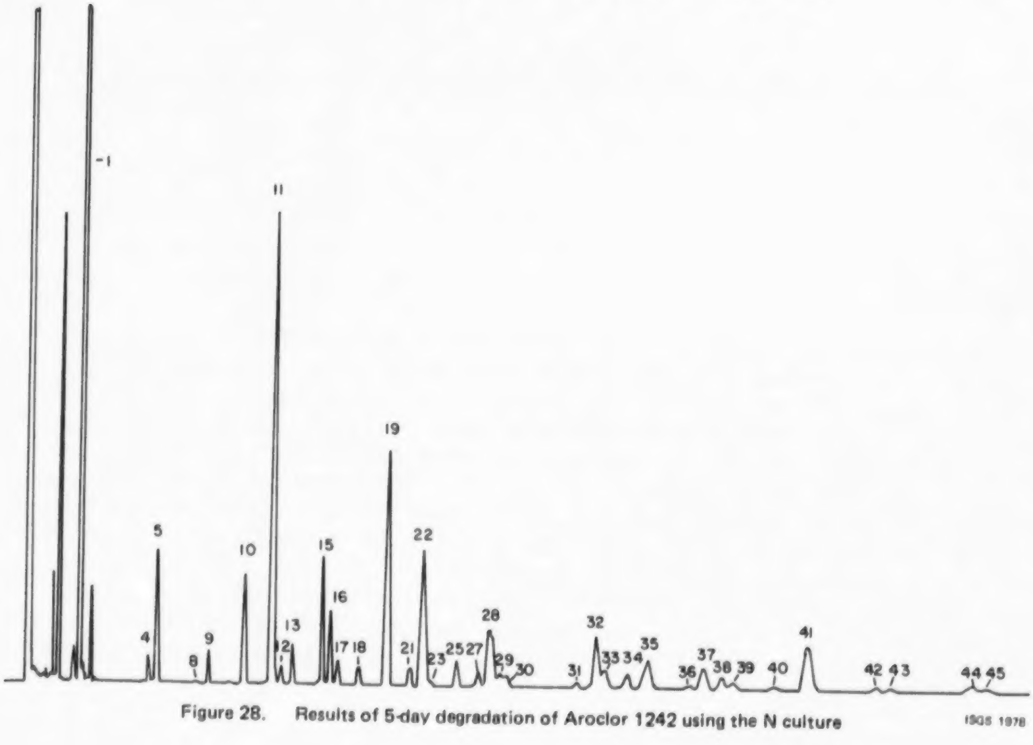

Figure 28. Results of 5-day degradation of Aroclor 1242 using the N culture

ISGS 1978

TABLE 19. Comparison of degradation of water-soluble Aroclor 1242 by the three mixed cultures of soil microorganisms.

		5-day degradation			15-day degradation		
Peak number	Number of Cl	C (%)	S (%)	N (%)	C (%)	S (%)	N (%)
2	1	100	100	100	100	100	100
3	1	100	100	100	100	100	100
4	2	64.8	100	30.9	71.5	100	25.3
5	2	57.3	93	98.6	61.7	99	100
6,7	2	98.7	100	100	100	100	100
8	2	-	100	99.3	99.5	100	100
9	2	97.2	99	99.7	97.9	99	99.9
10	3	12.6	88	0	3.8	89	0
11	3	19.8	67	98.7	17.3	71	100
12	3	38.5	-	45.7	21.4	-	54.8
13	3	48.4	90	15.2	34.9	89	0
14	2	100	-	75.2	100	-	78.2
15	2 + 3	41.9	71	39.3	42.8	78	45.8
16	3	73.2	99	86.9	77.0	99	96.8
17	3	7.4	100	22.0	0	100	0
18	3	77.8	98	100	80.6	100	100
19	3	51.3	96	93.9	53.9	98	98.4
20	3	100	-	100	100	-	100
21	3	2.9	-	0	0	-	0
22	4	21.9	72	99.2	18.7	76	100
23	4	-	-	-	0	-	0
24	4	100	99	60.9	100	99	70.3
25	4	7.2	72	0	0	73	0
26	3	100	100	100	100	100	100
27	4	99	90	100	0	90	100
28	4	8.5	42	20.1	0	56	13.0
29	4	25.2	-	-	0	-	21.6
30	4	-	-	0	0	-	0
31	4	9.7	38	27.3	31.8	43	0
32	4	8.1	34	55.6	0	49	80.2
33	4	0.7		55.6	0		62.8
34	4	0		0	0		0
35	4	0	39	37.0	0	67	38.2
36	4	19.4	-	-	22.5	-	0
37	3	3.7	38	17.5	0	51	0
38	4	0	44	37.9	0	45	100
39	4	20.3	81	37.9	49.4	85	0
40	3	25	15	0	-	0	0
41	4	0	30	47.9	0	43	62
42	4	0	-	-	-	-	-
43	4	0	-	-	-	-	-
44	4	0	-	21.3	-	-	-
45	4	17	-	21.3	76.1	-	-

could be a mixture of isomers. If it were a mixture, the isomers may have different degradation rates.

In order to calculate the amount of PCBs left at any particular time, the reaction order, *n*, and the rate constant, *K*, must be determined. The basic rate equation is

$$\frac{dC}{dt} = -KC^n$$

where C is the concentration of a compound, $\frac{dC}{dt}$ is the change in concentration with respect to time, t and K and n are as defined above. The equation can be rearranged to

$$\frac{dC}{C^n} = -Kdt$$

TABLE 20. Results of the kinetic study of the degradation of water-soluble Aroclor 1242 by the N culture.

		Percentage of degradation				
Peak number	Number of Cl	3 hrs. (%)	6 hrs. (%)	12 hrs. (%)	24 hrs. (%)	48 hrs. (%)
2	1	92.1	100	100	100	100
3	1	100	100	100	100	100
4	2	0	9.8	21.8	19.7	36.6
5	2	12.5	10.9	20.8	35.9	69.6
6,7	2	72.1	93.3	100	100	100
8	2	35.5	52.9	76.7	87.9	90.3
9	2	38.2	64.1	80	88.5	95.5
10	3	0	3.6	0	0	2.6
11	3	8.4	0	5.6	20.9	55.9
12	3	41.6	18.5	13.7	14.3	23.1
13	3	0	0	0	0	5.8
14	2	100	100	100	100	100
15	2 + 3	20.6	12.9	15.0	15.8	22.9
16	3	17.3	9.8	20.1	26.9	45.5
17,18	3	27.1	31.9	53.4	64.2	80.0
19,20	3	19.5	25.3	40.4	49.8	59.8
21,22	3	0	0	6.0	14.4	37.2
23	4	-	-	-	-	-
24	4	34.2	40.1	56.4	-	71.5
25	4	18.4	0	0	0	0
26	3	32.2	56.1	84.2	92.9	95.9
27	4	0	0	0	15.0	51.8
28,29,30	4	0	0	0	0	0
31	4	0	0	62.4	-	17.1
32	4	0	0	0	0	0
33	4	0	0	0	0	0
34	4	0	0	0	0	0
35	4	0	0	0	0	0
36	4	0	0	0	0	0
37	3	24.7	0	0	0	6.2
38	4	0	0	0	0	0
39	4	0	0	0	0	0
40	3	-	-	-	-	-
41	4	14.3	0	0	0	0
42	4	-	-	-	-	-
43	4	-	-	-	-	-
44	4	-	-	-	-	-
45	4	0	-	-	-	0

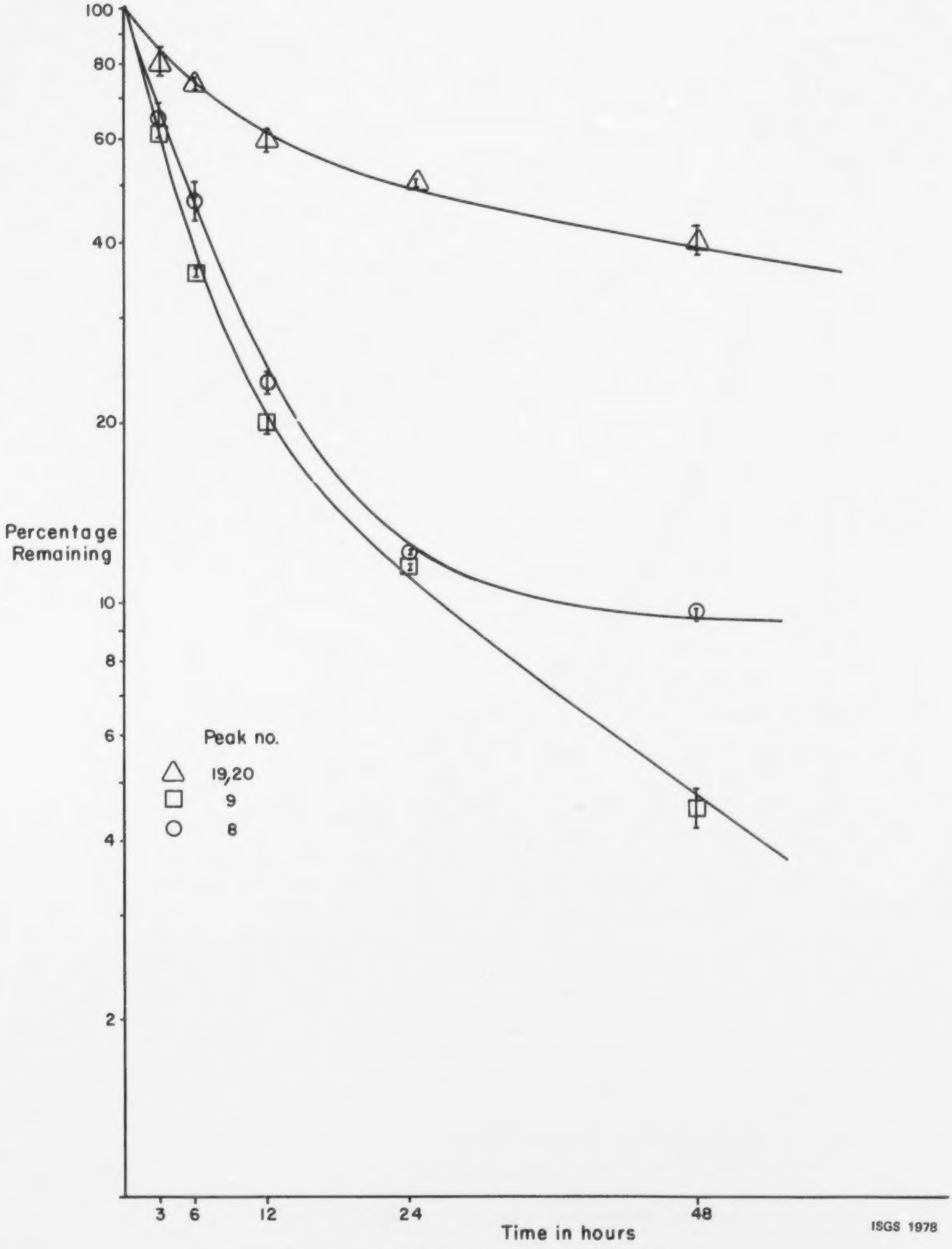

Figure 29. Degradation at timed intervals of selected PCB isomers

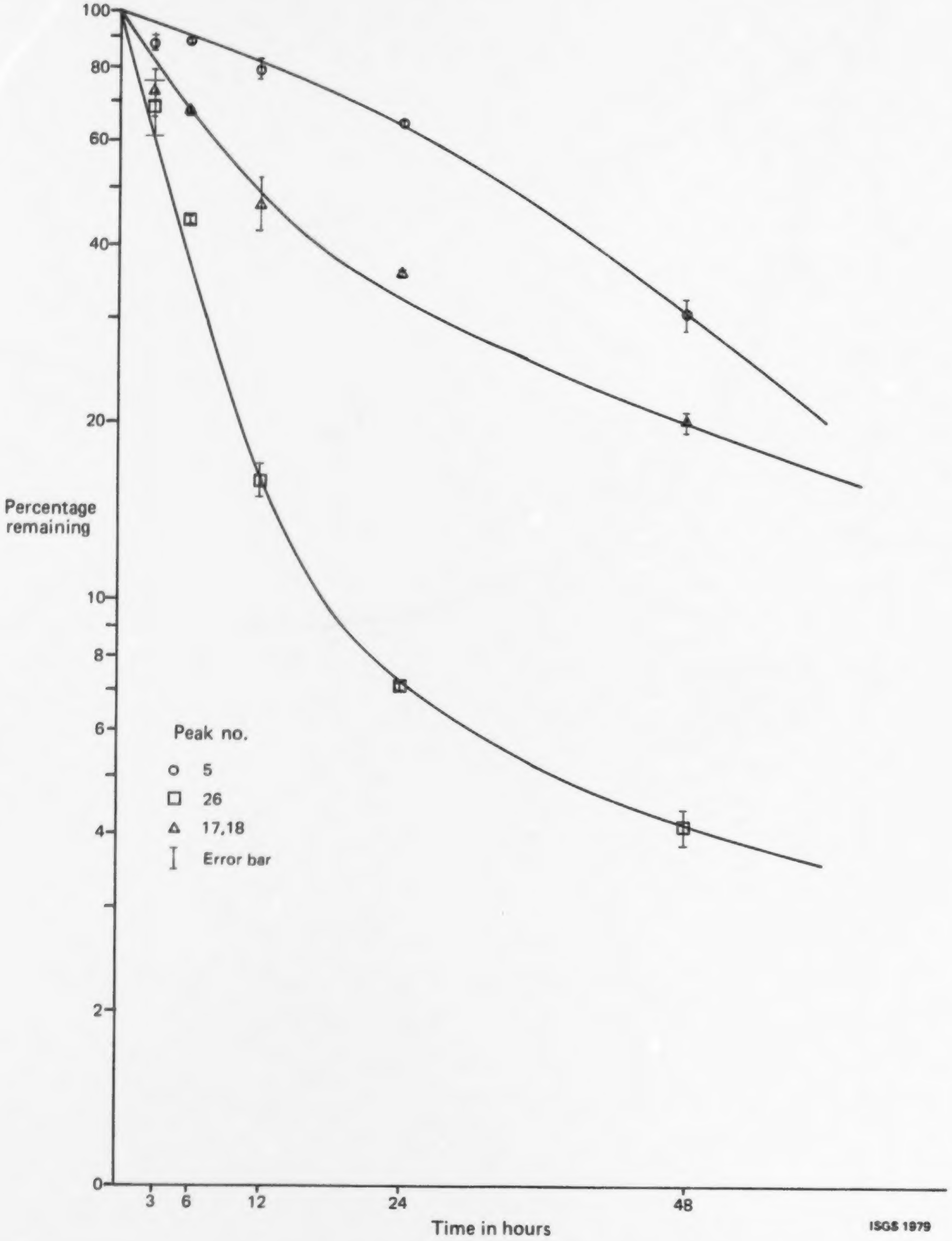

Figure 30. Degradation at timed intervals of selected PCB isomers

By integrating equation 3, we get equation 4

$$\frac{C_t^{\,1-n}}{1-n} - \frac{C_o^{\,1-n}}{1-n} = -Kt. \tag{4}$$

Rearranging this

$$C_t^{\,1-n} - C_o^{\,1-n} = (n-1)\ Kt \tag{5}$$

or

$$C_t^{\,1-n} = (n-1)\ Kt + C_o^{\,1-n}\ ; \tag{6}$$

the final equation is then

$$C_t = [(n-1)\ Kt + C_o^{\,1-n}]^{\frac{1}{1-n}}\ . \tag{7}$$

To determine the reaction order for the reduction of sample peaks 5, 8, 9, (17-18), (19-20), and 26 the following methods were used:

Since the basic rate equation is

$$\frac{dC}{dt} = -KC^n \tag{2}$$

then

$$\ln\left(\frac{dC}{dt}\right) = n \ln C + \ln K. \tag{8}$$

By plotting $\ln(\frac{-dC}{dt})$ vs. $\ln C$, the slope (n) and the intercept ($\ln K$) can be determined ($\frac{dC}{dt}$ was determined from the percentage remaining from Table 20; C was taken as the concentration midway between the two points used to determine a particular slope $\frac{dC}{dt}$).

Table 21 lists the K and n values for peaks number 5, 8, 9, (17-18), (19-20), and 26. The rate constant, K, was calculated using the percentage of PCB remaining at each time; therefore the units of K are (percentage remaining) $^{(1-n)}$per hour. C_o equals 100 percent at time zero. The constants in Table 21, when used in equation 7, yield answers that are within 5 percent of the experimental data.

Several things should be pointed out with regard to these numbers. First, the differential method used here to determine n and K is subject to errors because of the difficulties in determining the accurate values for $\frac{dC}{dt}$. This is especially applicable here because only 5 data points were used to calculate the line for determining n and K. However, the correlation coefficient (r) was very high (> 0.95) for all but two of the peaks. These two peaks, (17-18) and 5, had r values of 0.867 and 0.64 respectively. Also the closeness of the calculated numbers to the experimental data gives support to the calculated n and K values.

Second, the n value for peak (19-20) is very high. One would expect n values of 2 or less. The high n value may be due to the fact that this peak and (17-18) are a combination of two or more different PCB isomers. If the two or more isomers degrade at rapidly different rates, then the n value for the combined peak may be somewhat unusual. The n values, although they may not be a true reaction order for a particular isomer, do allow an empirical prediction using equation 7.

Cometabolization

PCBs are rarely found in isolation in the environment. There are usually more easily oxidizable chemicals such as acetic acid and amino acids available for the microorganisms to utilize. When microorganisms are utilizing one compound as an energy source, cometabolization of another compound may occur (Baxter et al., 1975; Horvath, 1972). Horvath (1972) described cometabolization as "the process in which a microorganism oxidized a substance without being able to utilize the energy derived from this oxidation to support growth."

TABLE 21. Rate constants and reaction orders for selected PCB isomers.

Peak number	Number of Cl	n	K (percentage remaining)$^{(1-n)}$/hr
5	2	0.347	3.44×10^{-1}
8	2	2.211	9.283×10^{-4}
9	2	1.747	7.24×10^{-3}
17,18	3	2.04	6.19×10^{-4}
19,20	3	3.72	2.92×10^{-7}
26	3	1.651	1.04×10^{-2}

Cometabolization of PCBs in the presence of sodium acetate was studied. Table 22 lists the results after 5 and 15 days of cometabolization and PCB degradation. Both cultures degraded PCBs to a large degree, but the cometabolization samples produced greatly enhanced degradation of the higher chlorinated PCB isomers and other hard-to-be-degraded isomers.

One possible reason for enhanced degradation of PCBs in the cometabolization samples could be due to the increased mass of microorganisms present. When the microorganisms are grown on PCBs alone, very little additional biomass is produced because of the limited amount of carbon source present in the solution. When acetic acid, or any easily degradable substrate, is present the microorganisms can grow on the acetic acid. While they are using the acetic acid they may oxidize the PCBs slightly. Because the total mass of microorganisms present has increased, this slight oxidization by each microorganism adds up to a more complete degradation for the entire system as a whole. This type of cometabolization will only work for cultures of microorganisms that are acclimated or selected to PCB degradation.

Another possible explanation is that the PCBs adsorbed onto the additional biomass in the cometabolization samples and were not extracted. This is a possibility because PCBs adsorb easily onto nonpolar surfaces such as bacterial cell walls. The sonification study showed that the PCBs could be extracted from the small amounts of biomass present in the samples containing only PCBs, but did not rule out the possibility of poor extraction in the presence of large amounts of biomass.

Soil and Sludge Extraction

Chromatograms of the soil and sludge extracts were compared to chromatograms of Aroclor 1242 and 1254. By this comparison the peaks in the extracts that were caused by PCB isomers were determined. Figure 15 shows a plot of relative area of the identified PCB peaks versus chromatograph retention time. If the PCBs were being degraded in the soil after application in the sludge, then there should be a buildup of the higher chlorinated isomers (those with longer retention times). In addition, there should be fewer of the lower chlorinated isomers in the soil. Each point on the graph represents a peak determined to be a PCB isomer. The number over the point is the percentage of degradation of that peak in the cometabolization study. The degradation from the cometabolization study was used because it would more closely represent the environmental situation where other organics are present.

As illustrated in Figure 31, the sludge has more low chlorine isomers than the soil, and the soil has relatively more high chlorine isomers than the sludge. This seems to indicate that there is degradation of some low chlorine isomers and an accumulation of the nondegradational higher chlorine isomers. The cometabolization degradation results agree in part with this conclusion. The two peaks at 25 and 28 minutes are not degraded and they build up in the soil, whereas the peak at 26 minutes is degraded and does not build up to the same extent. This pattern, however, is not obtained for the peaks at 15.5 and 23 minutes. This result may not be significant

TABLE 22. Co-metabolization of PCBs with sodium acetate by mixed culture microorganisms.

		Percentage of degradation			
		5 day		15 day	
Peak number	Number of Cl	PCB (%)	Cometab. (%)	PCB (%)	Cometab. (%)
2	1	100	100	100	100
3	1	100	100	100	100
4	2	54.5	86.0	45.5	78.2
5	2	99	99	100	100
6,7	2	100	100	100	100
8	2	100	100	100	100
9	2	100	100	100	100
10	3	0	5.0	6.4	9.9
11	3	96.8	100	100	100
12	3	96.8	100	98.6	100
13	3	8.2	38.9	10.4	68.9
14	2	100	100	100	100
15	2 + 3	32.9	90.4	58.9	95.4
16	3	96.8	100	100	100
17	3	0	0	0	0
18	3	100	100	100	100
19	3	96.7	100	100	100
20	3	100	100	100	100
21	3	9.1	0	0	0
22	4	95	97.4	90	90
23	4	95	97.4	100	100
24	4	24.6	100	57.4	100
25	4	0	0	0	0
26	3	100	100	100	100
27	4	100	100	100	100
28	4	8.0	62.2	35.2	91.2
29	4	8.0	100	35.2	100
30	4	0	11.0	0	0
31	4	4.6	19.1	0	77.6
32	4	50.8	100	78.1	100
33	4	50.8	100	78.1	100
34	4	0	0	0	22.1
35	4	48.1	100	64.3	100
36	4	0	15.4	13.6	35.9
37	3	0	15.4	13.6	36.9
38	4	100	100	100	100
39	4	1.1	61.7	38.7	100
40	3	0	0	20.6	0
41	4	52.2	100	75.2	100
42	4	0	0	0	0
43	4	0	0	0	0
44	4	0	0	0	0
45	4	0	50	0	50

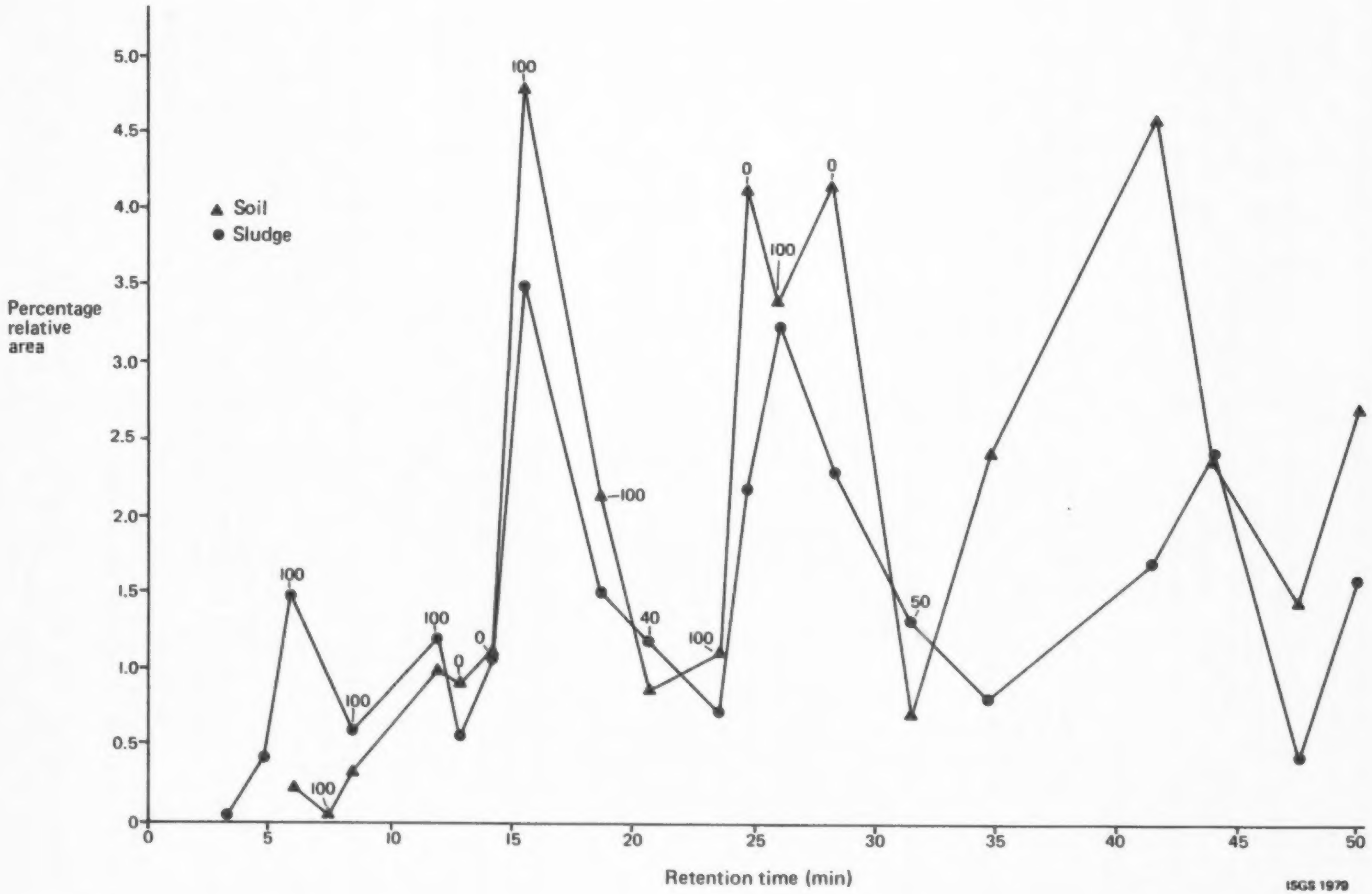

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Figure 31. Relative distribution of PCB isomers in the soil and sludge extracts with respect to retention time. The number over the points are the percentage degradation of that peak in the cometabolization study (table 22).

because different cultures have been shown in this study to degrade the various PCB isomers differently.

Several things could lead to error in this interpretation. First, the soil was dried in an oven, which may have volatilized some of the lower chlorine isomers. Second, the data are not quantitative in the sense that one cannot relate the total amounts of a PCB isomer in the sludge and how much sludge was applied to the amount of that PCB isomer found in the soil.

Other Observations

It has been noted that PCBs adsorb to glass surfaces (Gresshoff, Mahanty, and Gortner, 1977). In the blanks that were run in this study, however, no adsorption of PCBs was noted. One possible explanation of this is that when microorganisms are present in the water, the PCBs adsorb preferentially onto them rather than on the glass surface.

Several other points must be clarified when interpreting the results of this study. First, a mixed culture of microorganisms was used in contrast to the pure cultures of PCB-degrading microbes used by most other researchers (Lunt and Evans, 1970; Catelani et al., 1971, 1973; Gibson et al., 1973; Wallnofer et al., 1973; Ahmed and Focht, 1973a, 1973b; Baxter et al., 1975; and Furukawa, Tonomura, and Kamibayashi, 1978). Therefore, the more rapid degradation of PCBs found in this study compared to that previously reported may be partly attributed to the use of the mixed culture. In addition to the PCB-degrading microbes in such a culture, many other species of microorganisms may be present that could speed the degradation of the PCBs by removing potentially inhibitory intermediates. This mixed-culture approach is closer to the conditions that exist in the environment than a pure culture.

Second, only water-soluble PCBs were utilized. Water-soluble and total PCBs have different relative proportions of PCB isomers (Haque, Schmedding, and Freed, 1974). Therefore, the degradation of water-soluble PCBs is less than would be achieved for total PCBs. Because most potential migration of PCBs would be in an aqueous environment, the degradation of the water-soluble isomers are the most environmentally significant.

The PCB degradation studies all showed the same general trends of other research (Ahmed and Focht, 1973a, 1973b; Baxter et al., 1975; Furukawa, Tonomura, and Kamibayashi, 1978; Tucker, Saeger, and Hicks, 1975; Mihashi et al., 1975); namely, the lower chlorinated isomers, in general, were more easily degraded than higher chlorinated ones, and different isomers with the same number of chlorines degraded at different rates. *But perhaps most significant in this study is that PCBs can be degraded to a large extent in a short period of time by mixed cultures of microorganisms.* In addition, if a PCB-degrading culture is used, the microbes will cometabolize PCBs while using another compound as a source of energy.

Because two of the mixed cultures were enriched from soil or sediment that contained PCBs, and because it appears that there were already PCB-degrading microbes present, PCBs are expected to be degraded to some extent in the environment. Koeman et al. (1969) pointed out that most PCB residuals in animals yield GC chromatographs similar to Aroclor 1260, a rather highly chlorinated series of PCB isomers. This has also been noted by other researchers (Smith, K. E., Illinois Natural History Survey, personal communication) since then. Because Aroclor 1242, a relatively lower chlorinated series of isomers, accounted for the majority of PCBs produced and marketed (HEW, 1972), it would appear that the lower chlorinated isomers are degraded in the environment to some extent.

The isolation from soil or sediment of microorganisms that can degrade PCBs readily suggests the possibility of their future inoculation into wastes containing PCBs before disposal, or biological digestion prior to disposal.

SECTION 9

EFFECT OF HUMIC ACID AND SOIL ON VOLATILIZATION OF PCBs FROM WATER[1]

RESULTS AND DISCUSSION

PCBs are known to have low solubility in water (MacKay and Wolkoff, 1973) and to have a pronounced tendency to adsorb on particulate matter (Griffin et al., 1978). The aromatic character of PCBs is believed to cause them to be adsorbed onto humic substances by hydrophobic interactions. Though the structure of humic acid is still under extensive investigations, a major portion of humic acid is speculated to be constructed by crosslinked phenolics and thus to have a distinct aromatic character.

The PCB volatility measurements given in table 23 show that water-soluble humic acid attenuated the volatility of PCBs from aqueous solution. The attenuation does not seem to be very effective, however, because as much as 500 mg/L of humic acid were needed to reduce the volatility to 73 percent of that of the control, that is, from pure water as shown by the chromatograms in Figure 32.

Recent evidence (Reuter and Havlicek, 1978) has indicated that humic acids are composed predominantly of an aliphatic substructure (about 70 percent), whereas the aromatic moiety was actually present in the structure as only about 20 to 30 percent of the total composition. This new structural information about humic acid explained the experimental observation that relatively few PCBs were adsorbed by dissolved humic acids. Because the binding of PCBs to humic acid in aqueous solution is relatively weak, the PCBs in solution and those bound to humic acid actually formed a dynamic

TABLE 23. Relative amount of PCB volatilized from water containing humic acid or soil compared to control.

Control	50 mg/L humic acid	500 mg/L humic acid
100%	87%	73%

Control	1000 mg/L (47.30)[a] Catlin soil	5000 mg/L (236.5)[a]	6400 mg/L (302.7)[a]
100%	86%	50%	21%

[a] The numbers in parentheses indicate mg/L of total organic C content.

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[1] Authors: Hsi Meng, E.S.K. Chian, and R. A. Griffin

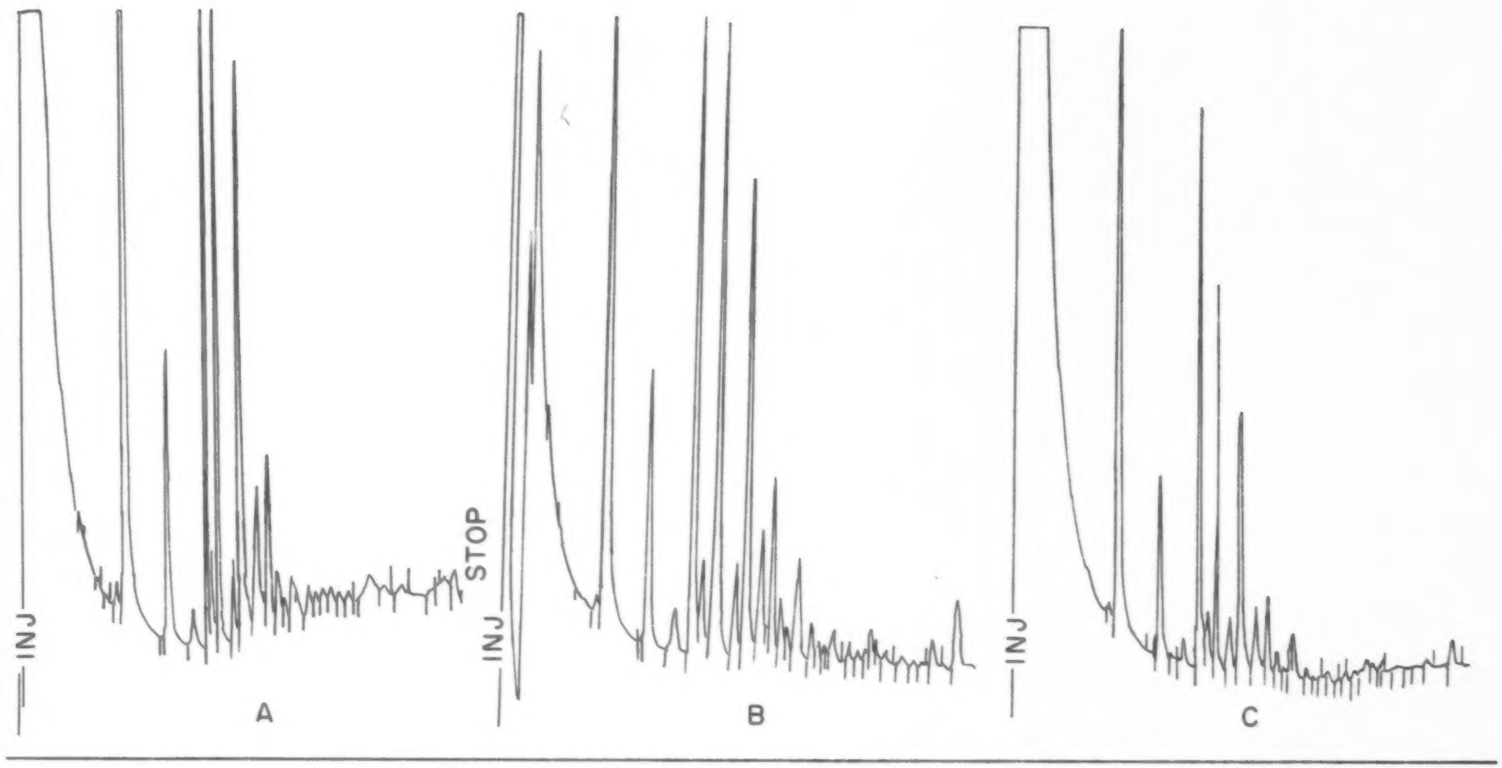

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Figure 32. Comparison of attenuation of volatilized PCBs by dissolved humic acid addition. (A) Control. (B) 50 mg/L dissolved humic acid added. (C) 500 mg/L dissolved humic acid added.

equilibrium. Therefore, the binding of PCBs by soluble humic substances does not substantially reduce the concentration of free PCBs. The volatilization of PCBs is thus not effectively influenced by the presence of soluble humic acids at a pH of 12; however, this may not be the case when the humic acid is present as colloids at a lower pH. Adsorption of dissolved PCBs on the particulate and nonionized molecules, such as humic substances, is expected to be far more effective than that on the ionized molecules in true solution; this observation is based on the results of this study of PCB adsorption onto Catlin soil and soluble humic acid.

Attenuation of the volatility of water-soluble PCBs by soil adsorption resulted in a greater reduction of the volatile fractions of PCBs from the aqueous solution (Table 23) than was the case for the soluble humic acid. This analysis was based on the total organic content in the solution (see the numbers in parentheses in Table 23). Therefore, the binding of PCBs to solids does seem to effectively reduce the amount of PCB volatilized as shown by the results of the Catlin soil addition (Table 23). Thus the adsorption of PCBs on the particulate matter was more effective than that on the soluble humic matter as shown by the chromatograms in Figure 33. Table 24 compares our earlier soil adsorption study (Griffin et al., 1978) to the soil volatility attenuation study presented here.

As indicated in Table 24, the results of volatilization and adsorption are parallel in that for each the attenuation was more efficient by adding a larger amount of soil. This correlation further implies that attenuation of PCB volatilization is directly related to binding of the PCBs to the soil solids by an adsorption mechanism.

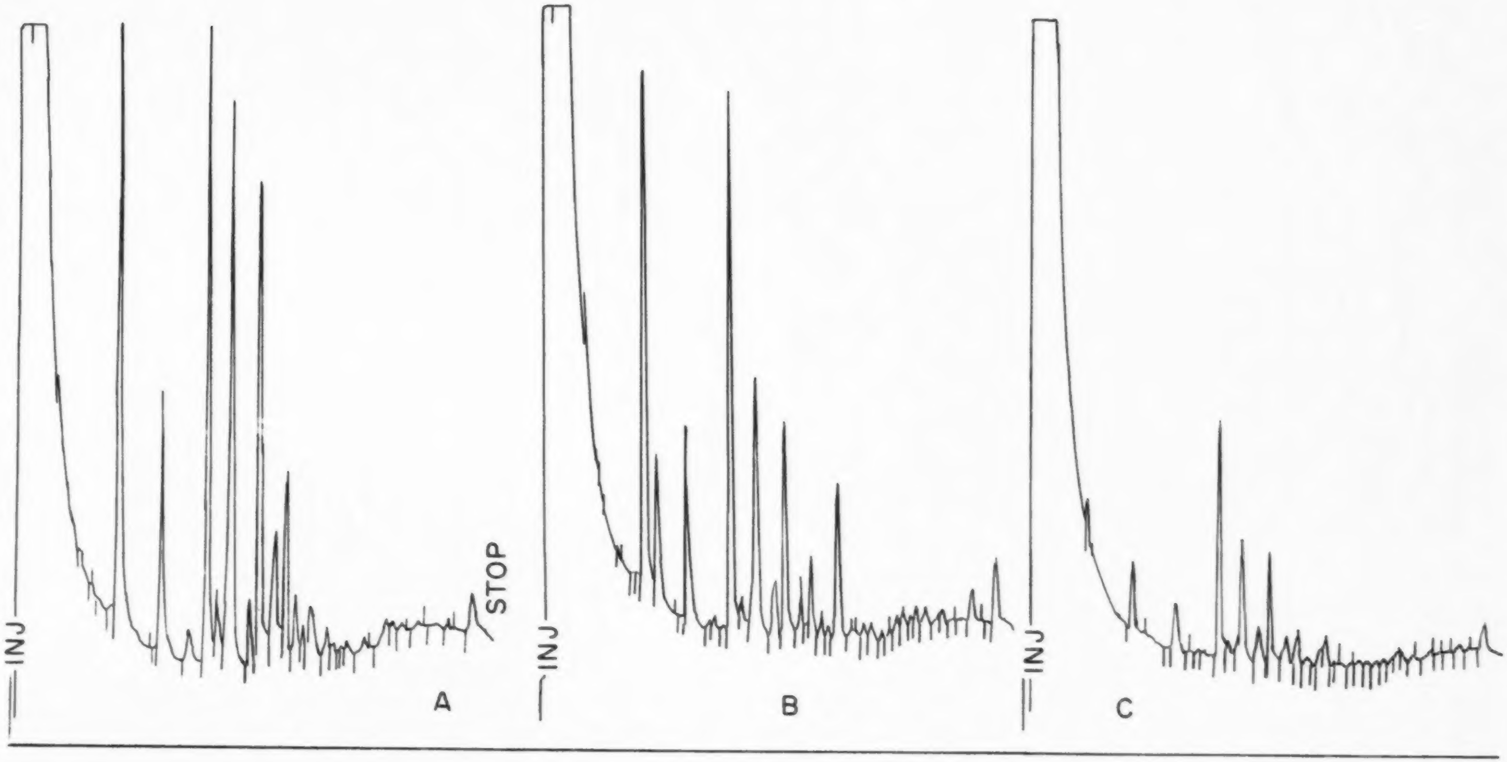
The conditions of this experimental study were somewhat different than would be expected under field conditions; however, a water-logged soil could result in a condition that resembles those conditions. Also a landfill site producing leachate may closely resemble the conditions of our experiments with humic acid, because an appreciable amount of soluble humic substances has been found in landfill leachates (Chian, 1977).

Change in Composition of the Volatile PCBs

The percentage of lower-chlorinated PCBs in the samples was evaluated. The early-eluting larger peaks in the chromatograms (Figs. 32 and 33) represented the more volatile and lower-chlorinated PCBs. The area under

TABLE 24. The relative attenuation of volatilization of PCBs by soil as compared with the attenuation due to adsorption from solution by the same soil.

	1000 mg/L Catlin soil (%)	5000 mg/L (%)	6400 mg/L (%)
Adsorption attenuation	85	55	42
Volatilization attenuation	86	50	21



ISGS 1978

Figure 33. Comparison of attenuation of volatilized PCBs by soil addition (see figure 32 for the control). (A) 1000 mg/L Catlin soil added. (B) 5000 mg/L Catlin soil added. (C) 6400 mg/L Catlin soil added.

these GC peaks was summed up and compared with the total area of all the GC peaks in the chromatogram. The results of direct injection of PCB standards dissolved in hexane containing 500 ppm Aroclor 1242 showed 52 percent lower-chlorinated PCBs, whereas purging of water saturated with PCBs yielded 80 percent lower-chlorinated PCBs in the traps. By adding 50 mg/L of humic acid, 82 percent of the lower-chlorinated PCBs were found in the traps. Addition of 500 mg/L of humic acid yielded 87 percent of the lower-chlorinated PCB isomers in the trap. By the same token, the percentages of lower-chlorinated PCBs found in the traps after soil additions were 80, 79, 74 and 73 percent, respectively, with 0, 1000, 5000, and 6400 mg/L soil additions.

The higher-chlorinated PCBs were adsorbed more effectively by the soluble humic acids; this can be explained by the strong hydrophobic bonding of the PCBs to the humic substances. The affinity of higher-chlorinated PCBs to the humic substances is reflected by an increased volatile portion of the lower-chlorinated isomers; however, the soil addition experiments showed a small decrease and a leveling off of the amount of PCBs in the traps in the lower-chlorinated form. This is speculated to be due to limited penetration of the smaller lower-chlorinated isomers into pores of the interlayer and edge regions of clay minerals contained in the Catlin soil, and thus a slightly more efficient retention against volatilization.

The most visible change in isomer distribution comes from comparing the hexane-soluble PCBs and water saturated with PCBs. This can be explained by the higher volatility of the lower-chlorinated isomers and their higher solubility in water.

Comparison with Theoretical Volatilization Process

MacKay and Wolkoff (1973) predicated the half-life of Aroclor 1242 volatilized from water to be 6 hours. Therefore, the quantity volatilized in 20 minutes would correspond to 3 percent of the Aroclor added to the purging flask used in this study. They pointed out that the high activity coefficient of a sparingly soluble compound in water favors a high rate of evaporation. The experimental conditions of this study agreed with the basic assumptions outlined by MacKay and Wolkoff (1973). When 0.5 μg of PCBs were introduced into water followed by purging, the amount of PCBs volatilized was found to be 0.5 percent. The trapping efficiency was found to be 71 percent as evaluated by concentrating a known amount of PCB in hexane and following the same analytical protocol. Thus, the actual evaporation efficiency was 0.7 percent. Since 1 μL of the 5 μL solution was introduced onto the GC column, 0.7 percent times 5 gives the total evaporation efficiency of 3.5 percent. This agrees well with the value of 3 percent volatilized from pure water based on the theoretical calculation of MacKay and Wolkoff's (1973) model. Similar calculations for the other experiments allow for comparisons. For example, volatilization of PCBs from solutions containing 500 mg/L humic acid was reduced to 2.6 percent, and volatilization was reduced to 0.74 percent from suspensions containing 6400 mg/L soil.

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